IMPERIAL INSTITUTE

OF

AGRICULTURAL RESEARCH, PUSA.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, December 5th, 1918, at 8 p.m., Professor W. J. Pope, C.B.E., F.R.S., President, in the Chair.

It was announced that the Society had lost, through death, the following Fellows:

Killed in Action.

	Elected.	Died.
John Percy Batey	May 15th, 1913.	April 4th.

Died.

James Mason Crafts	Dec. 1st, 1870.	June 1917.

Certificates were read for the first time in favour of:

Pierre Beghin, 86, Market Street, St. Andrews.
John Joseph Bryant, 28, Greenwood Road, Dalston, E. 8.
George Butterworth, 107, Burlington Street, Ashton-under-Lyne.
William Harold Squier Cheavin, 70, Somerset Road, Huddersfield.
Edward Charles Cull, B.Sc., 31, Bourne Street, Dudley.
John Campbell Earl, 161, South Street, St. Andrews.
Algie Hancock, 3, North Street, St. Andrews.
George Samuel Heaven, B.Sc., Templemead, Albany Road, Coventry.
James Rintoul-Higham, Overmore, Richmond Road, E. Twickenham.
Frederick William Hodkin, B.Sc., 28, Thoresby Road, Hillsborough, Sheffield.
Richard Edward [illegible]uston, 504, Lordship Lane, Dulwich, S.E. 22.
Francis Frederick Mooney, 39, Queen's Place, Summerseat, Manchester.
Albert Riley, B.Sc., Westfield Lodge, Thorner, Leeds.
Hugh Vernon Thompson, M.A., Croft House, Garden Village, Stoke-on-Trent.
Greatrex Johnson Woods, 52, Burrard Road, West Hampstead, N.W. 6.

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PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

JOURNAL
OF
THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Mandeliminohydrin*.*

By JOHN EDWIN MACKENZIE.

THE amides of monobasic organic acids are generally represented as having the constitution $R\cdot CO\cdot NH_2$. To the isomeric formula, $R\cdot C(OH){:}NH$, the name iminohydrin has been applied and a large

* NOTE BY JAMES WALKER.—The circumstance that the iminohydrins are good conductors of electricity and are at the same time practically neutral in aqueous solution renders these substances of great interest from the point of view of the theory of amphoteric electrolytes (*Proc. Roy. Soc.*, 1904, **73**, 155; **74**, 271). Some years ago I accordingly prepared glycolliminohydrin and lactiminohydrin in a state of purity and investigated some of their physico-chemical properties. From measurements of the degree of hydrolysis of glycolliminohydrin hydrochloride by the methods of methyl acetate catalysis and of electromotive force, it appeared that in $N/8$-solution the salt was hydrolysed to the extent of about 50 per cent. The degree of hydrolysis of the sodium salt of glycolliminohydrin, judged from its electrical conductivity, was at the same concentration also about 50 per cent. The results with lactiminohydrin were similar. From these determinations it was possible to calculate the molecular conductivity of the iminohydrins themselves by means of the theory of amphoteric electrolytes. The calculated value indicated that the iminohydrins should be very feeble conductors of electricity, and bore no sort of relationship to the conductivity actually observed, which is high and roughly that of a salt.

The natural conclusion to draw was that the iminohydrins are not in reality amphoteric electrolytes, and that the formula usually attributed to them is erroneous. However, as the two examples investigated were of a very similar nature, it seemed desirable to study other members of the class, and at my request Dr. J. E. Mackenzie began their preparation. Other duties, however, compelled him to relinquish the work, which was then taken up by Dr. H. G. Rule, and carried to a successful conclusion, the true nature of the iminohydrins being disclosed.

ing compounds, from their analysis and apparent unimolecular condition in aqueous solution, were represented as having the constitution $R\cdot C(OH)\colon NH$, isomeric with the acid amides.

Thus the formation of glycolliminohydrin, the first of these compounds to be obtained from the corresponding ethyl ether hydrochloride, was explained according to the equation

$$OH\cdot CH_2\cdot C(OEt)\colon NH,HCl + AgOH = OH\cdot CH_2\cdot C(OH)\colon NH + AgCl + EtOH,$$

the iminohydrin, together with a large proportion of glycollamide, being supposed to result from the direct hydrolytic action of the water present. In addition to the above, lactiminohydrin and α-hydroxy*iso*butyriminohydrin were prepared and very shortly described.

The chief characteristics of these compounds, as noted by Eschweiler, are their high melting points, fusion being generally accompanied by decomposition, the liberation of ammonia by alkalis, and their peculiar reaction towards certain metallic salts, the glycollic compound, for example, slowly giving a deposit of calcium glycollate on the addition of a solution of calcium chloride. The latter action was supposed to take the course

$$2OH\cdot CH_2\cdot C(OH)\colon NH + CaCl_2 + 2H_2O = (OH\cdot CH_2\cdot CO_2)Ca + 2NH_4Cl.$$

Eschweiler further states that the iminohydrins are basic in character, and claims to have isolated definite hydrochlorides of the general type $R\cdot C(OH)\colon NH,HCl$, which are neutral in aqueous solution.

The failure of all attempts to effect an interconversion between the iminohydrins and their apparent isomerides, the acid amides, led to an extended investigation by Hantzsch (*Ber.*, 1901, **34**, 3142), who showed that these compounds were comparatively strong electrolytes, having in reality a molecular weight double that assigned to them by Eschweiler. In opposition to the latter author, Hantzsch finds the iminohydrin hydrochloride to be strongly hydrolysed in aqueous solution, and also comments on the fact that all the known iminohydrins are derivatives of α-hydroxy-acids.* In spite of numerous attempts, however, he was unable to prepare other types. In explanation of the discovery that the iminohydrins were electrolytes of the general formula $(R\cdot CO\cdot NH_2)_2$, they were represented as having the constitution $NH\colon CR\cdot O\cdot NH_2\colon CR\cdot OH$, the complex being supposed to ionise in aqueous solution into the ions $(NH\colon CR\cdot O)'$ and

* In a patent application Eschweiler makes the bare claim to have prepared acet- and benz-iminohydrins, but no further details are given.

$(NH_2\dot{:}CR\cdot OH)^{\cdot}$. The failure to establish any relationship to the acid amides, despite the similarity between the structure of these compounds and that suggested above for the iminohydrins, was met by Hantzsch with the statement that "amides and *iso*amides (iminohydrins) are not isomerides, but polymerides, and their relations are therefore different from those of genuine tautomerides, which possess equal molecular weights." The hydrochloride of glycolliminohydrin was nevertheless formulated as

$$OH\cdot CH_2\cdot C(OH)\dot{:}NH_2Cl,$$

in which case we should have a true isomeride of glycollamide existing in combination with hydrochloric acid.

More recently, the behaviour in solution of glycolliminohydrin, lactiminohydrin, and their salts has been examined by Professor James Walker (see Note to preceding paper), with results which led him to the conclusion that these compounds are not true amphoteric electrolytes, and that the formula assigned to them by Hantzsch is incorrect. For this reason, and since all previous attempts to prepare iminohydrins other than α-hydroxy-derivatives had failed, pointing to the possibility that the hydroxyl group was an integral part of the molecule, the following investigation was undertaken.

Several representatives of this class have been prepared and examined, and all were found to possess the high molecular weight and saline properties characteristic of glycolliminohydrin. The early preparation of the methoxyacetic and the phenylacetic derivatives showed that the formation of an iminohydrin was in no way dependent on the presence of an α-hydroxy-group in the molecule of the interacting imino-ether. Subsequently, an examination of the comparatively stable mandelic compound * led to the discovery that the iminohydrins are complex amidine salts of the general formula $R\cdot C(NH_2)\dot{:}NH,R\cdot CO_2H$. This was confirmed by the synthesis of mandeliminohydrin (mandelamidine mandelate) from mandelamidine hydrochloride and sodium mandelate,

$$C_6H_5\cdot CH(OH)\cdot C(NH_2)\dot{:}NH,HCl + C_6H_5\cdot CH(OH)\cdot CO_2Na =$$
$$C_6H_5\cdot CH(OH)\cdot C(NH_2)\dot{:}NH,C_6H_5\cdot CH(OH)\cdot CO_2H + NaCl,$$

and of Eschweiler's original glycolliminohydrin (glycollamidine glycollate) from the corresponding amidine hydrochloride and sodium glycollate,

$$OH\cdot CH_2\cdot C(NH_2)\dot{:}NH,HCl + OH\cdot CH_2\cdot CO_2Na =$$
$$OH\cdot CH_2\cdot C(NH_2)\dot{:}NH,OH\cdot CH_2\cdot CO_2H + NaCl.$$

In connexion with the latter synthesis, for which glycollamidine

* See preceding paper by J. E. Mackenzie.

hydrochloride had first to be prepared, some of Eschweiler's work on the iminohydrin (amidine) salts has been repeated and several inaccuracies have been corrected.

From the above point of view, a review of the properties of the "iminohydrins" presents no peculiarities. Evidence of saline character is furnished by high melting points, insolubility in ether or hydrocarbons, and by high electrical conductivities in aqueous solution, the latter in the case of the glycollic compound being very little short of the value for a typical salt such as sodium acetate. The reaction with metallic salts is seen to be an example of ordinary double decomposition, that between glycolliminohydrin and calcium chloride following the course

$$2OH\cdot CH_2\cdot C(NH_2):NH,OH\cdot CH_2\cdot CO_2H + CaCl_2 = 2OH\cdot CH_2\cdot C(NH_2):NH,HCl + (OH\cdot CH_2\cdot CO_2)_2Ca.$$

The soluble substance left in solution is glycollamidine hydrochloride, and not ammonium chloride, as assumed by Eschweiler, and later by Hantzsch. Characteristic of amidine salts is the disruption which accompanies fusion and the readiness with which ammonia is evolved on treatment with alkalis, whilst the decomposition suffered by the iminohydrins in general on heating with aqueous solvents is due to hydrolysis of the amidine into amide and ammonia. This is well illustrated in the case of the phenylacetic compound, where attempted crystallisation from alcohol was found to lead to the production of phenylacetamide and ammonium phenylacetate,

$$CH_2Ph\cdot C(NH_2):NH,CH_2Ph\cdot CO_2H + H_2O = CH_2Ph\cdot CO\cdot NH_2 + CH_2Ph\cdot CO_2NH_4.$$

The contradictory statements of Eschweiler and Hantzsch in connexion with the neutrality of the "iminohydrin salts" are also made clear, since these authors believed that the iminohydrin, $(R\cdot C(OH):NH)_2$, was capable of uniting with two molecules of hydrochloric acid to yield two molecules of the salt,

$$R\cdot C(OH):NH,HCl.$$

The hydrochloride, in reality an amidine salt, as isolated by Eschweiler, proved to be neutral when dissolved in water, whilst hydrolysis measurements carried out by Hantzsch with a solution containing one molecular proportion of iminohydrin to two of hydrochloric acid naturally led to the conclusion that the salt was considerably hydrolysed. The organic acid which is liberated in the latter case remains practically non-ionised in the presence of the excess of hydrochloric acid, thus accounting for the apparent dissociation values of 50 per cent. obtained by Walker (see Note to preceding paper) for glycolliminohydrin and lactiminohydrin

hydrochlorides, and by the author for the methoxyacetic and mandelic derivatives.

Mechanism of the Interaction of Imino-ethers and Water.

Pinner, in his monograph on the imino-ethers ("Die Imidoäther und ihre Derivate"), states that these compounds decompose slowly on keeping, generally giving rise to the alcohol and nitrile from which they are derived. In some cases the nitrile may polymerise on being liberated, whilst in others the decomposition may take place in a different manner and lead to the formation of an acid amide. An example of the latter type is furnished by α-hydroxy*iso*butyrimino-ethyl ether (Pinner, *loc. cit.*, p. 37), which on attempted distillation decomposes into the corresponding amide and alcohol, and it is probable that the interaction between benzimino-ethyl ether and water to form cyaphenin (Mackenzie, P., 1913, **29**, 175) is due to the initial formation and subsequent polymerisation of benzonitrile.

In those reactions where water is present, however, other changes may take place. Imino-ethers are at once strongly alkaline and readily hydrolysable compounds, and the work of Pinner has shown that the imino- and alkyloxy-groupings are extremely sensitive to attack, the actual group or groups affected depending on the reagent employed. In particular, ammonia reacts with imino-ether hydrochlorides with great readiness to form amidine salts. Although in no single instance was any trace of free ammonia observed during the above interactions between imino-ether and water, it was found by experiment that the addition of an equivalent of ammonium mandelate to an aqueous suspension of mandelimino-ethyl ether not only doubled the yield of amidine mandelate, but the deposition of the salt commenced almost immediately after the addition had been made. It seems probable, then, that in the interaction of imino-ethers and water, the first step is autohydrolysis of a portion of the substance in the alkaline medium to form the ammonium salt of the corresponding acid,

$$R\cdot C(OEt){:}NH + 2H_2O = R\cdot C(ONH_4){:}O + EtOH.$$

This salt, then, reacts with more free imino-ether to give the amidine salt or iminohydrin,

$$R\cdot C(ONH_4){:}O + R\cdot C(OEt){:}NH = R\cdot C(NH_2){:}NH,R\cdot CO_2H + EtOH.$$

In this connexion, Pinner, in describing the formation of amidine hydrochloride from imino-ether hydrochloride and a slight excess of alcoholic ammonia, remarks on the precipitation of

ammonium chloride, which then slowly dissolves with the formation of the soluble amidine salt.*

The production of amide is probably caused by direct hydrolysis of imino-ether and amidine in the alkaline solution, and the amount formed in any given experiment does not appear to bear any constant relation to that of the amidine salt.

EXPERIMENTAL.

The method of preparation adopted by Eschweiler, and later by Hantzsch, in which the imino-ether hydrochloride is added in small portions at a time to an equivalent amount of silver oxide suspended in water, led to such small and variable yields that its use was abandoned. Yields of 30—35 per cent. were obtained by allowing the free imino-ethers to remain with excess of water for some days at the ordinary temperature. During this time, the originally strong alkaline reaction of the imino-ether gradually disappeared, and a mixture of iminohydrin and acid was produced. At first the iminohydrin was isolated by repeated crystallisation from a suitable solvent. In some later cases, the dried products of reaction were extracted with ether in a Soxhlet apparatus, the insoluble iminohydrin being left behind in a comparatively pure state.

"Glycolliminohydrin" (glycollamidine glycollate) was prepared in a 30 per cent. yield by dissolving glycollimino-ethyl ether in excess of water and allowing the solution to remain for ten or twelve days. On evaporation to dryness in a vacuum over sulphuric acid, and repeated recrystallisation of the residual solid from alcohol, the pure iminohydrin was obtained in well-defined plates melting and decomposing at 166—168°. Eschweiler (*loc. cit.*) gives 161—162°.

In the hope of isolating some definite oxidation or reduction product, an electrolysis of the iminohydrin in aqueous solution was carried out in a divided cell. An analysis of the electrode gases, however, indicated complete disruption of the iminohydrin molecule. Similarly, all attempts by chemical means to isolate a basic or acidic component other than ammonia or glycollic acid, both of which were believed to be products of hydrolysis, led to no result.

Earlier attempts to prepare acet- and benz-iminohydrins were also unsuccessful (compare Hantzsch, *loc. cit.*, and Mackenzie, P., 1913, **29**, 175), the only recognisable products of reaction in the

* Since the above was written, a paper has been published by A. Knorr (*Ber.*, 1917, **50**, 229), in which the author claims to have shown conclusively that free ammonia does not react with free imino-ethers, but that amidine hydrochlorides are formed from them by reaction with ammonium chloride.

case of benzimino-ethyl ether being benzamide, cyaphenin, and a little ethyl benzoate. The first indication that the presence of an α-hydroxy-group was not an essential condition for the formation of an iminohydrin was given by the preparation of methoxyacetiminohydrin.

Methoxyacetimino-ethyl Ether, $CH_3 \cdot O \cdot CH_2 \cdot C(O \cdot C_2H_5):NH$.

Methoxyacetonitrile (29 grams), prepared from paraformaldehyde according to Wedekind's method (*Ber.*, 1903, **36**, 1383), was dissolved in ether and treated with an equivalent (24 c.c.) of absolute alcohol. The solution was cooled in ice, and dry hydrogen chloride (15 grams) passed in. After a short time, the liquid separated into two layers, and subsequently methoxyacetimino-ethyl ether hydrochloride crystallised out.

Some of the hydrochloride (16 grams) was shaken with ether and a concentrated solution of potassium carbonate. Much carbon dioxide was evolved, and the ethereal extract, after drying over sodium sulphate, was distilled. The boiling point of the distillate slowly rose to 136°, where it remained constant. The yield of methoxyacetimino-ethyl ether (b. p. 136°) was 5·5 grams.

The imino-ether is a colourless liquid with a peculiar odour; it is alkaline to litmus and miscible in all proportions with water. Ammonia is readily evolved on treatment with alkalis:

0·1789 gave 0·3381 CO_2 and 0·1474 H_2O. C=51·52; H=9·22.

$C_5H_{11}O_2N$ requires C=51·25; H=9·47 per cent.

It is probable that the substance was not quite pure, since all imino-ethers decompose to some extent on heating. An attempt to purify a portion by distillation under 50 mm. pressure gave a distillate passing over at 66—67°. This specimen on analysis proved to be no purer than the above.

"*Methoxyacetiminohydrin*" (*methoxyacetamidine methoxyacetate*) was obtained by allowing the free imino-ether (12 grams), mixed with excess of water, to remain at the ordinary temperature for five weeks. The water was removed in a vacuum over sulphuric acid, and the resulting mixture recrystallised repeatedly from alcohol containing about a third of its volume of benzene. The iminohydrin (2·2 grams) was obtained in large, well-shaped needles melting at 162—164°:

0·1835 gave 0·2715 CO_2 and 0·1332 H_2O. C=40·35; H=8·06.

$C_6H_{14}O_4N_2$ requires C=40·42; H=7·93 per cent.

It is readily soluble in alcohol and moderately so in water. In ether or benzene it dissolves sparingly. On heating with aqueous sodium hydroxide, ammonia is evolved.

Molecular Weight in Aqueous Solution (Cryoscopic Method).

Using 20 grams of solvent, the following data were obtained ($K = 1870$):

0·1225 gave $\Delta^t = -0{\cdot}129^\circ$. M.W. = 89.
0·2481 ,, $\Delta^t = -0{\cdot}250^\circ$. M.W. = 93.
0·3067 ,, $\Delta^t = -0{\cdot}309^\circ$. M.W. = 93.

$C_6H_{14}O_4N_2$ requires M.W. = 178, hence at the above dilutions the substance is almost completely ionised

Electrical Conductivity in Water at 25°.

The following determinations were made, using electrodes covered with a deposit of "grey" platinum, and to reduce still further errors arising from the oxidation at the electrodes, the electrolyte at each dilution was freshly prepared from a stock solution by the addition of the requisite amount of water ($\mu_{25} = 1{\cdot}6 \times 10^{-6}$).

An $N/20$-solution was prepared by dissolving 0·8907 gram of the "iminohydrin" up to 100 c.c.

v	20	40	100	200	400	1000	2000
μ_{25}......	60·9	64·0	67·8	69·8	70·8	71·6	72 0

At dilution $v = 2000$ oxidation was noticeable, as shown by the dropping of the cell-resistance. The figures show methoxyacetiminohydrin to be a good electrolyte, with a conductivity at high dilutions comparable with that of glycolliminohydrin, for which Hantzsch finds $\mu_{25} = 79{\cdot}5$ at $v = 2048$.

Hydrolysis of "Methoxyacetiminohydrin Hydrochloride."

According to Eschweiler and Hantzsch, the iminohydrins form hydrochlorides of the general type $R{\cdot}C(OH){:}NH,HCl$, salts which are considerably hydrolysed in aqueous solution. Walker (see Note to preceding paper) finds this hydrolysis in the case of the glycollic and lactic derivatives to approximate to 50 per cent. in $N/8$-solution.

The hydrolysis at the same dilution of methoxyacetiminohydrin hydrochloride was measured by the methyl acetate catalysis method, and found in this case also to be almost exactly 50 per cent.

Experiments directed towards the preparation of the unsubstituted "iminohydrins" corresponding with benzoic, phenylacetic, and acetic acids met at first with no success. As has been already stated, benzimino-ethyl ether reacts with water to give cyaphenin, and failure in the cases of phenylacet- and acet-imino-ethyl ethers was subsequently found to be due to hydrolysis of the "imino-

hydrins" during attempted purification by crystallisation. The two latter compounds were eventually obtained from the crude reaction mixture after removing the accompanying acid amide by extraction with ether in a Soxhlet apparatus.

"*Acetiminohydrin*" (*Acetamidine Acetate*),
$CH_3 \cdot C(NH_2):NH,CH_3 \cdot CO_2H$.

Acetimino-ethyl ether hydrochloride, prepared from acetonitrile (37·5 grams), alcohol, and hydrogen chloride in the usual manner, was converted into the free imino-ether by shaking with ether and a concentrated solution of potassium carbonate. The bulk of the ether was cautiously removed on the water-bath, and the residual liquid mixed with excess of water in a stoppered bottle. After ten weeks, the still faintly alkaline solution was evaporated to dryness in a vacuum over sulphuric acid, and the solid residue extracted with ether in a Soxhlet apparatus. The residue, melting at 66—148°, was partly soluble in benzene, the solution depositing crystals of acetamide (m. p. 79—82°). The insoluble portion, amounting to 3 grams, melted at 155—175°. The latter was purified by solution in cold alcohol and precipitation with benzene, giving a final product melting and decomposing at 185—187°.

All attempts to recrystallise it from warm alcohol or ethyl acetate, with or without the addition of benzene, resulted in the decomposition of the iminohydrin.

Qualitative tests showed that this substance was a good electrolyte, whilst its high melting point, insolubility in ether, and the evolution of ammonia with sodium hydroxide, showed it to be of the same class of substances as glycolliminohydrin. Owing to the low yield and its unstable nature, it was not further examined.

"*Phenylacetiminohydrin*" (*Phenylacetamidine Phenylacetate*),
$C_6H_5 \cdot CH_2 \cdot C(NH_2):NH,C_6H_5 \cdot CH_2 \cdot CO_2H$.

Free phenylacetimino-ethyl ether, prepared from phenylacetonitrile (Pinner, "Die Imidoäther," p. 66), was allowed to remain in contact with water at the ordinary temperature for several weeks. The semi-solid mass was filtered, and the solid portion, after drying, extracted with ether in a Soxhlet apparatus. After thirty hours' extraction, the iminohydrin was left behind in a pure state, melting and decomposing at 227—230°:

0·1586 gave 0·4138 CO_2 and 0·0974 H_2O. C = 71·13; H = 6·82.

$C_{16}H_{18}O_2N_2$ requires C = 71·10; H = 6·72 per cent.

By solution in ethyl acetate and precipitation with benzene, a product of the original melting point was obtained in very fine

needles. The substance is very sparingly soluble in water, soluble in alcohol, and insoluble in benzene or ether. With aqueous alkalis, ammonia is readily evolved, and the compound is of the same unstable nature as acetiminohydrin, attempted recrystallisation from alcohol or water leading to partial decomposition into amide and the ammonium salt of the corresponding acid. For this reason, it was not further examined.

The four "iminohydrins" described above, derivatives of glycollic, methoxyacetic, acetic, and phenylacetic acids, were not suited to a detailed investigation on account of their instability towards solvents and their general physical properties. A more convenient subject for examination was found in "mandeliminohydrin."

"*Mandeliminohydrin*" (*Mandelamidine Mandelate*), $C_6H_5\cdot CH(OH)\cdot C(NH_2){:}NH,C_6H_5\cdot CH(OH)\cdot CO_2H$.

This compound had already been obtained in small quantities by Mackenzie (see preceding paper) by the interaction of aqueous silver oxide and mandelimino-ethyl ether hydrochloride. In the preparation of larger quantities, it was obtained from benzaldehyde as follows.

Moist potassium cyanide (80 grams) was placed in a flask and covered with an ethereal solution of one equivalent (106 grams) of benzaldehyde. The whole was cooled in ice, and rather less than one equivalent (50 c.c.) of concentrated hydrochloric acid added slowly with constant shaking. The ethereal solution was decanted and dried for twenty-four hours over anhydrous sodium sulphate, after which it was poured off and cooled in ice. Equivalent amounts of alcohol (46 grams), and dry hydrogen chloride (36·5 grams) were added, and after a short time the liquid became almost solid, owing to the separation of mandelimino-ethyl ether hydrochloride. In a few hours the latter (135 grams) was collected.

The hydrochloride was suspended in ether and shaken with a concentrated solution of potassium carbonate. On removal of the ethereal layer and evaporation of the solvent in a vacuum, the free imino-ether (87 grams) remained as a white solid.

The imino-ether was introduced into a stoppered bottle containing excess of water, and the latter placed in a shaking machine. After five or six days, the bulk of the solid suddenly passed into solution, when the reaction mixture was removed and the water evaporated in a vacuum over sulphuric acid. The dry residue was transferred to a Soxhlet apparatus and extracted for some hours with ether, leaving an insoluble portion melting and decomposing at about 180° which, after one crystallisation from alcohol,

gave the pure iminohydrin (25 grams), melting and decomposing at 185—187°. Mackenzie quotes 173—179° (see preceding paper), the actual figure depending very much on the rate of heating.

Mandelamidine mandelate crystallises in colourless plates, insoluble in ether, benzene, or light petroleum, sparingly soluble in water (100 grams dissolve 1·87 grams at 25°), rather more readily so in ethyl alcohol, and moderately so in methyl alcohol (100 grams dissolve 4·80 grams at 25°). It is comparatively unaffected by solvents, and can be recovered from them unchanged, whereas glycolliminohydrin recovered, for example, from a solution in hot alcohol, has always a decidedly lower melting point than the starting material.

Molecular Weight in Aqueous Solution (Cryoscopic Method).

Using 20 grams of solvent, the following data were obtained (K = 1870):

0·1210 gave $\Delta^t = -0·073$. M.W. = 155.
0·2348 ,, $\Delta^t = -0·147$. M.W. = 149.

$C_{16}H_{18}O_4N_2$ requires M.W. = 302, hence at these dilutions the compound is almost completely ionised.

In boiling methyl alcohol (pure anhydrous), the following figures were obtained, using an electrically heated modification of Beckmann's apparatus, jacketed in a vacuum tube.

Weight of alcohol taken, 27·91 grams (K = 860).

0·5340 gave E = 0·080. M.W. = 206.
0·9923 ,, ,, = 0·150. M.W. = 204.
1·384 ,, ,, = 0·214. M.W. = 200.

As was to be expected, these figures indicate partial ionisation only of the compound in methyl alcohol.

Electrical Conductivity in Water at 25°.

As in the case of methoxyacetiminohydrin, the electrodes used were coated with "grey" platinum, but at the higher dilutions, $v = 400$ and above, oxidation was made apparent by the falling resistance of the cell. The solution at each dilution was freshly made up from an *N*/20-stock solution containing 1·511 grams in 100 c.c. The water used had a specific conductivity value of $1·4 \times 10^{-6}$ at 25°.

v	20	40	100	200	400	1000	2000
μ_{25}......	43·0	46·0	51·0	53·0	54·4	55·2	56·2

"Mandeliminohydrin Hydrochloride."

The hydrolysis in aqueous solution of the "hydrochloride of glycolliminohydrin" was measured by Hantzsch by determining the electrical conductivity of a solution containing one molecular proportion of the bimolecular "iminohydrin" and two molecular proportions of hydrogen chloride. The figures obtained indicated extensive hydrolysis. As already stated, Walker, using the methyl acetate catalysis method, found almost exactly 50 per cent. of the hydrogen chloride in the uncombined state in *N*/8-solution. The hydrolysis of the mandelic compound, determined by the latter method, was again found to be 50 per cent. in *N*/16-solution. On the other hand, Eschweiler states (compare Hantzsch, *Ber.*, 1901, **34**, 3154) that glycolliminohydrin hydrochloride, obtained by evaporation of the solution of iminohydrin in hydrochloric acid, is a neutral salt having the structure $OH \cdot CH_2 \cdot C(OH){:}NH,HCl$.

"Mandeliminohydrin," on being treated with excess of aqueous hydrochloric acid and evaporation in a vacuum over solid potassium hydroxide, was found to retain exactly a half-equivalent of acid, which could be estimated by titration with standard alkali in the presence of methyl-red. This solid hydrochloride showed no definite melting point, but "mandeliminohydrin," when dissolved in hot dilute hydrochloric acid, deposited, on cooling, well-formed crystals of a hydrochloride melting at 215—219°. These crystals proved to be neutral in aqueous solution, and evolved much ammonia with sodium hydroxide.

Action of Alkalis on "Mandeliminohydrin."

In the course of some experiments on the action of alkalis on "mandeliminohydrin," an aqueous solution of the latter was treated with exactly one molecular equivalent of sodium hydroxide. No ammonia could be detected after remaining for some minutes in the cold, but on warming the strongly alkaline solution, a considerable evolution of the gas was observed. The mixture was boiled until the evolution of ammonia ceased, when the residual liquid was found to be neutral. On cooling, a crop of crystals was deposited melting at 128—132°. These, after crystallisation from alcohol, melted at 131—132°, and proved to be pure mandelamide. The aqueous mother liquor contained sodium mandelate and yielded free mandelic acid on acidification. No other product could be detected.

These results suggested that the basic portion of the iminohydrin was set free by alkali and subsequently decomposed with

evolution of ammonia. Attempts to isolate a base soluble in ether were only successful when the aqueous alkali originally in use was replaced by a saturated solution.

When the finely powdered iminohydrin was rapidly shaken in a separating funnel with ether and saturated aqueous potassium hydroxide, the ethereal layer left, on evaporation in a vacuum, a very small amount of a white solid. This substance melted at 98—110°, was soluble in water, giving a powerfully alkaline solution, and after a short time decomposed, with the evolution of much ammonia. These properties are those of an amidine, mandelamidine, $C_6H_5\cdot CH(OH)\cdot C(NH_2){:}NH$ (Beyer, *J. pr. Chem.*, 1885, [ii], **31**, 383), melting at 110°. The neutral hydrochloride melting at 215—219° obtained above should then correspond with mandelamidine hydrochloride, $C_6H_5\cdot CH(OH)\cdot C(NH_2){:}NH,HCl$, which melts at 213—214° (Beyer). A specimen of the latter prepared from mandelimino-ethyl ether hydrochloride and alcoholic ammonia was found to melt at 219—220°.

The behaviour of "mandeliminohydrin" towards acids and alkalis, coupled with the characteristic reaction of glycolliminohydrin with calcium chloride, resulting in the deposition of calcium glycollate, pointed to these compounds being, in reality, amidine salts of the general type $R\cdot C(NH_2){:}NH,R\cdot CO_2H$.

Synthesis of "Mandeliminohydrin."

This constitution was readily confirmed by the formation of the "iminohydrin" on mixing in warm aqueous solution equivalent amounts of mandelamidine hydrochloride and sodium mandelate. On cooling, the solution deposited hard nodules melting and decomposing at 175—180°, which, after recrystallisation from alcohol, showed the characteristic plate formation of "mandeliminohydrin," and melted and decomposed at 184—186°.

Synthesis of "Glycolliminohydrin."

Equivalent amounts of sodium glycollate and glycollamidine hydrochloride (for preparation, see later) were mixed in aqueous solution. After evaporating to dryness, extraction with alcohol removed "glycolliminohydrin," melting at 166—168°.

"p-*Chloromandeliminohydrin*" (p-*Chloromandelamidine* p-*Chloromandelate*), $C_6H_4Cl\cdot CH(OH)\cdot C(NH_2){:}NH,C_6H_4Cl\cdot CH(OH)\cdot CO_2H$.

This compound was prepared for the purpose of comparing its physical constants with those of the mandelic derivative before the

constitution of the iminohydrins as amidine salts had been established. The preparation was a somewhat lengthy process, starting with the conversion of *p*-chlorotoluene into *p*-chlorobenzylidene chloride, $C_6H_4Cl{\cdot}CHCl_2$, by the action of chlorine on the boiling liquid under the influence of rays from a "Uviol" mercury-vapour lamp. The chloro-compound was heated in a sealed tube at 170° with water, yielding *p*-chlorobenzaldehyde, and the latter extracted with ether. The ethereal solution, after drying over sodium sulphate, was used direct for the preparation of p-*chloromandelimino-ethyl ether*, $C_6H_4Cl{\cdot}CH(OH){\cdot}C(OEt){:}NH$, by the method used above for the mandelic compound. Owing to the great tendency of the chloroaldehyde to oxidise in air, it was found necessary to carry out the reaction in closed vessels in an atmosphere of carbon dioxide. Twenty-four grams of *p*-chlorobenzylidene chloride gave 8 grams of the free imino-ether.

The compound crystallised from ether in well-defined plates melting at 107—109°. When recrystallised from light petroleum, it melted at 108—110°.

The crude product tends to oxidise in air, becoming red, but the pure substance can be kept for some weeks without much discoloration. It is sparingly soluble in water, soluble in dilute hydrochloric acid or alcohol, and readily so in hot benzene, from which it is precipitated by light petroleum.

An attempt to determine the chlorine content by Stepanov's method, using alcohol and metallic sodium, led to too high a figure being found, and it was noticed that decomposition of the imino-ether had taken place in such a way as to lead to the production of hydrogen cyanide.

Using the Carius-Volhard method, the following figures were obtained: 0·1172 gram was heated in a sealed tube with 0·2242 gram of silver nitrate and 2 c.c. of fuming nitric acid. After the reaction, the oxides of nitrogen were removed and the unchanged silver nitrate was titrated with thiocyanate, of which 7·35 c.c. (0·1052*N*) were required:

Cl = 16·5.

$C_{10}H_{12}O_2NCl$ requires Cl = 16·6 per cent.

"Chloromandeliminohydrin" was prepared, in small quantity only, by the method adopted in the case of the mandelic derivative. Continuous extraction of the dry product with ether separated the mixture into two portions.

p-*Chloromandelamide*, $C_6H_4Cl\cdot CH(OH)\cdot CO\cdot NH_2$.

The ethereal extract deposited a white, crystalline substance which, on crystallisation from benzene, melted at 122—123°. Analysis showed this to be the expected *p*-chloromandelamide. On hydrolysis with alkali, it yielded ammonia and a salt of chloromandelic acid.

0·1162 Gram heated with 0·2626 gram of silver nitrate and fuming nitric acid required for titration 9·10 c.c. of *N*/10-thiocyanate. Cl = 19·4.

$C_8H_8O_2NCl$ requires Cl = 19·1 per cent.

The amide is soluble in alcohol, sparingly so in ether, and very sparingly so in benzene. p-*Chloromandelamidine* p-*chloromandelate* was left behind in the crude state after extraction with ether as a white powder melting at 170—180°. Recrystallisation from a mixture of alcohol and benzene raised the melting point to 186—195° (with decomposition).

This compound proved to be unexpectedly unstable, and very readily decomposed with the evolution of ammonia on heating with solvents. Owing to its instability and the fact that its percentage composition does not differ from that of the amide with which it is liable to be contaminated, it was not further examined.

Treatment with dilute hydrochloric acid and subsequent recrystallisation from alcohol yielded the crystalline p-*chloromandelamidine hydrochloride*, $C_6H_4Cl\cdot CH(OH)\cdot C(NH_2)\!:\!NH,HCl$, melting and decomposing at 252—253°:

0·3360 required 15·20 c.c. *N*/10-$AgNO_3$. Cl′ = 16·04

$C_8H_9ON_2Cl,HCl$ requires Cl′ = 15·97 per cent.

Amidine Salts.

Some compounds of this type have been described by Eschweiler under the heading of "iminohydrin salts," but since much of the data furnished by this author is inaccurate, and since, moreover, he was under a misapprehension as to the structure of the compounds with which he was dealing, it was thought desirable to repeat certain of the preparations.

Glycollamidine Hydrochloride, $OH\cdot CH_2\cdot C(NH_2)\!:\!NH,HCl$.

Eschweiler (*ibid.*) describes glycolliminohydrin hydrochloride as being prepared by the evaporation of a solution of the iminohydrin in an equivalent amount of dilute hydrochloric acid. The re-

crystallised product is quoted as melting at 135° and having the structure $OH·CH_2·C(OH):NH,HCl$.

Glycollamidine glycollate, prepared from the free imino-ether by treatment with water, gave, on evaporation with hydrochloric acid, a crude product melting at 130—150°. After repeated purification by solution in hot alcohol and precipitation with benzene, the hydrochloride was obtained in very fine needles melting at 150—151°.

In larger quantities, this salt was prepared from glycolliminoethyl ether hydrochloride and alcoholic ammonia according to the general method recommended by Pinner (*loc. cit.*). After purification from 98 per cent. alcohol, a product of the above melting point was obtained.

0·2003 was distilled with excess of sodium hydroxide and the ammonia trapped in 25 c.c. of 0·2036 *N*-sulphuric acid. The excess of acid required 7·70 c.c. of 0·1934 *N*-sodium hydroxide. N = 25·17.

0·1037 treated with 20 c.c. of *N*/10-silver nitrate required for titration 10·65 c.c. of *N*/10-ammonium thiocyanate. Cl = 31·97.

$C_2H_6ON_2,HCl$ requires N = 25·34; Cl = 32·08 per cent.

The salt is sparingly soluble in alcohol and practically insoluble in benzene or ether. It is very readily soluble in water and deliquescent in air.

Glycollamidine Sulphate, $(OH·CH_2·C(NH_2):NH)_2,H_2SO_4$.

Glycollamidine hydrochloride was treated with an equivalent of sulphuric acid, and the excess of water evaporated on the steam-bath. Recrystallisation from aqueous alcohol gave the sulphate in colourless leaflets melting and decomposing at 205°. Eschweiler (*loc. cit.*) gives 150° as the melting point of glycolliminohydrin sulphate, prepared in a similar manner:

0·2042 gave 0·1900 $BaSO_4$. S = 12·78.

$(C_2H_6ON_2)_2H_2SO_4$ requires S = 13·02 per cent.

The salt is not deliquescent, is readily soluble in water, and very sparingly so in absolute alcohol.

Glycollamidine Hydrogen Sulphate, $OH·CH_2·C(NH_2):NH,H_2SO_4$.

In order to ascertain if Eschweiler's sulphate, melting at 150°, were the hydrogen sulphate, glycollamidine hydrochloride was treated in aqueous solution with exactly two equivalents of sulphuric acid and evaporated to dryness in a vacuum over sodium hydroxide and sulphuric acid. The product was quite free from

chloride, and, after drying on porous porcelain in a vacuum, melted at 65—67° after having softened at 63°. On recrystallisation from aqueous alcohol, leaflets melting at 150—175° were deposited, which proved on analysis to contain more than 90 per cent. of the normal sulphate. Even from solvents containing a large excess of acid, the crystals deposited were mainly of the normal salt.

Glycollamidine Nitrate, $OH{\cdot}CH_2{\cdot}C(NH_2){:}NH,HNO_3$.

This substance was obtained by evaporating on the steam-bath equivalent amounts of glycollamidine hydrochloride and aqueous nitric acid. Recrystallisation from aqueous alcohol gave the pure nitrate, melting at 110—111° (Eschweiler gives 95° as the melting point of glycolliminohydrin nitrate).

A product melting at 110—111° was also obtained from glycollamidine glycollate (iminohydrin) and nitric acid:

0·2330 gave 0·1504 CO_2 and 0·1074 H_2O. C=17·58; H=5·15.
0·1497 ,, 39·10 c.c. N_2 (dry) at 10·5° and 747 mm. N=30·88.
$C_2H_6ON_2,HNO_3$ requires C=17·52; H=5·15; N=30·68 per cent.

The salt is very readily soluble in water, and practically insoluble in absolute alcohol, benzene, or ether. From aqueous alcohol, it is deposited in leaflets which are stable in air.

Eschweiler's "lactiminohydrin sulphate" (lactamidine sulphate) is correctly quoted as melting at about 198°. A specimen prepared from the "iminohydrin" was found to melt and decompose at 200—202°. The hydrochloride and nitrate have already been described by Pinner.

Summary.

(1) The iminohydrins or *iso*amides, formulated by Eschweiler as $R{\cdot}C(OH){:}NH$, and by Hantzsch as $NH{:}CR{\cdot}O{\cdot}NH_2{:}CR{\cdot}OH$, have been shown to be amidine salts of the general type

$$R{\cdot}C(NH_2){:}NH,R{\cdot}CO_2H.$$

This structure has been confirmed by the synthesis of the mandelic compound and of Eschweiler's original "glycolliminohydrin."

(2) It is suggested that the production of amidine salt by the reaction between imino-ether and water takes place mainly through the intermediate formation of the ammonium salt of the corresponding acid, which by subsequent reaction with free imino-ether gives rise to the amidine salt.

(3) Certain inaccuracies of Eschweiler in reference to "iminohydrin" (amidine) salts have been corrected.

In conclusion, I desire to express my thanks to Professor Walker, at whose suggestion the above work was undertaken, for the interest he has shown throughout its course. I am also indebted to the Earl of Moray Research Fund for a grant which has covered most of the expenses in connexion with this research.

CHEMISTRY DEPARTMENT,
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III.—*The Preparation of α-Naphtholphthalein.*

By EMIL ALPHONSE WERNER.

BY heating phthalic anhydride with α-naphthol for a short time to the boiling point of the latter, Grabowski (*Ber.*, 1871, **4**, 661) obtained what was apparently an anhydride of α-naphtholphthalein. This substance, which had the composition $C_{28}H_{16}O_3$, was insoluble in alkalis, and was of no particular interest.

The true phthalein ($C_{28}H_{18}O_4$), which is readily soluble in alkalis with the production of an intense pure blue colour, was shortly afterwards obtained by Grabowski (*Ber.*, 1871, **4**, 725; 1873, **6**, 1065) from the interaction of α-naphthol and phthalyl chloride.

Sörensen and Palitzsch (*Biochem. Zeitsch.*, 1910, **24**, 381) have directed attention to the great delicacy of α-naphtholphthalein as an indicator in alkalimetry, and have described in detail a method for its preparation, which differs but little from that recorded by Grabowski.

Having recently received a request from one of my colleagues for a small quantity of this indicator, which apparently is difficult to procure at the present time, a few experiments were made in order to ascertain if the substance could be prepared with the aid of phthalic anhydride, which is so generally employed in the preparation of other phthaleins.

Conditions necessary for obtaining the compound in very good yield were soon established, and since α-naphtholphthalein has some special application in biochemistry, it may be of interest, and a saving of time, to others to place on record the following details of its preparation.

The most successful experiment was conducted as follows. An intimate mixture of 7 grams of α-naphthol and 3·8 grams of powdered phthalic anhydride was introduced into a stout, wide-mouthed test-tube, and 0·75 c.c. of concentrated sulphuric acid was

added. The tube, which carried a thermometer, was partly immersed in a beaker half full of water, and heat was applied until the contents of the tube had reached 60°; the heating was maintained for four hours, during which period the temperature was never allowed to rise above 65°. The mixture was well stirred at intervals by means of the thermometer.

The dark greenish-black, viscous product was extracted with water until free from sulphuric acid, after which the semi-solid mass was digested at about 70° with a litre of 0·5 per cent. solution of sodium hydroxide until the extraction of all material soluble in the alkali had been completed. The weight of pale yellow, insoluble matter (Grabowski's 'anhydride') was only 0·8 gram. To the deep blue solution obtained, after filtration, dilute hydrochloric acid in quantity sufficient to neutralise about one-half of the sodium hydroxide present was added, after which the liquid was saturated with carbon dioxide. The pale reddish-brown precipitate of α-naphtholphthalein was collected, washed, redissolved in dilute solution of sodium hydroxide, and reprecipitated as before. The weight obtained after drying in a vacuum over sulphuric acid was 2·3 grams, equal to nearly 33 per cent. of the weight of α-naphthol taken. Sörensen and Palitzsch, using phthalyl chloride, obtained a yield equal to 30·5 per cent. calculated on the same basis.

In order to ensure a successful result in the preparation of α-naphtholphthalein by the method just described, great care must be taken to avoid a rise of temperature above 65°. Thus, when the temperature was maintained at 70—80°, the yield was only about one-half of that obtained at 65°, whilst at 80—90°, Grabowski's 'anhydride' was almost the sole product.

Excess of sulphuric acid was also found greatly to promote the formation of the anhydride at the expense of the phthalein.

Attempts to hydrolyse Grabowski's anhydride to α-naphtholphthalein by heating with dilute acids or alkalis under the ordinary pressure or in sealed tubes were unsuccessful.

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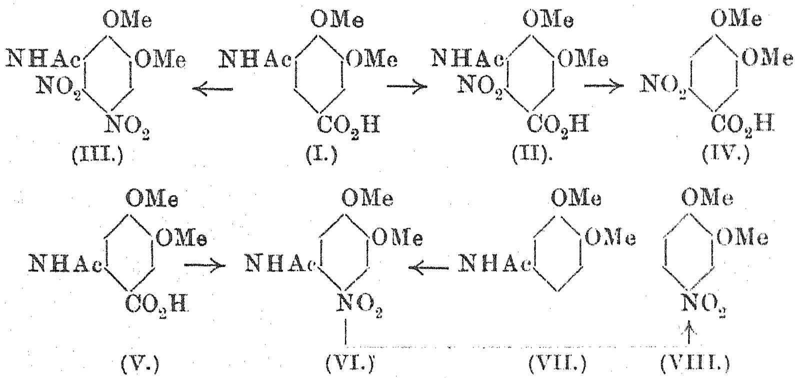
IV.—*The Nitration of 5- and 6-Acetylamino-3:4-dimethoxybenzoic Acids and 4-Acetylamino-veratrole.*

By John Lionel Simonsen and Madyar Gopala Rau.

The nitration of 2-acetylamino-3:4-dimethoxybenzoic acid and 3-acetylaminoveratrole was investigated by Gibson, Simonsen, and Rau (T., 1917, **111**, 69), and in view of the results obtained it appeared to us desirable to examine the products formed by the nitration of the two isomeric acetylamino-3:4-dimethoxybenzoic acids and of 4-acetylaminoveratrole.



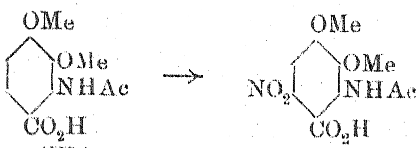
5-*Acetylamino*-3:4-*dimethoxybenzoic acid* (I), which was found to be most conveniently prepared from 5-nitrovanillin under the conditions described in the experimental part of this paper, when treated with nitric acid gave a mixture of a nitroacetylamino-acid and a neutral substance which was insoluble in sodium carbonate solution. The latter substance was found to be 4:5-dinitro-3-acetylaminoveratrole (III), a substance already described (*loc. cit.*, p. 78). The nitroacetylamino-acid was readily shown to be 6-*nitro*-5-*acetylamino*-3:4-*dimethoxybenzoic acid* (II), since the *amino*-acid obtained from it on hydrolysis yielded, when diazotised in alcoholic solution, 6-nitroveratric acid (IV).

When 6-*acetylamino*-3:4-*dimethoxybenzoic acid* (V) was nitrated, it was not found possible to avoid the displacement of the carboxyl group, and the sole product of the reaction was 5-*nitro*-4-*acetylaminoveratrole* (VI). The same substance was also obtained by the nitration of 4-acetylaminoveratrole (VII). The constitution of the nitroacetylaminoveratrole was proved by the fact that when

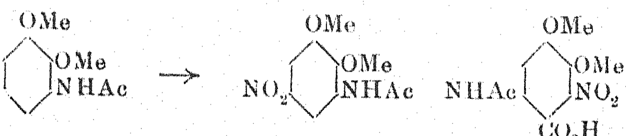
the amino-group was displaced by hydrogen, 4-nitroveratrole (VIII) was obtained.

If these results are considered in the light of the suggestions made by the authors (T., 1917, **111**, 224), it will be observed that the nitration of 5-acetylamino-3:4-dimethoxybenzoic acid proceeds exactly as might be expected. In the formation of the nitroacetylamino-acid, which is evidently the primary product of the reaction, the negative carboxyl group appears to exercise no direct orientating effect except in so far as it neutralises the methoxy-group in the para-position with respect to it; the first nitro-group enters the ortho-position with respect to the acetylamino-group and the para-position with respect to the second methoxy-group. There appears to be no tendency for the elimination of a methoxy-group to take place, as has been observed by various investigators in somewhat analogous cases, and further nitration of the nitroacetylamino-acid merely results in the displacement of the carboxyl group with the formation of 4:5-dinitro-3-acetylaminoveratrole.

The result obtained in the case of the 6-acetylamino-acid was somewhat unexpected. In view of the fact that both in the case of 2-acetylamino-3:4-dimethoxybenzoic acid (IX) and of 3-acetylaminoveratrole (X) the nitro-group enters the para-position with respect to the methoxy-group which was in the ortho-position with respect to the acetylamino-group, it was thought that the 6-acetylamino-acid would yield the 2-nitro-derivative (XIII).



(IX.) (XI.)



(X). (XII.) (XIII.)

This did not prove to be the case, displacement of the carboxyl group by the nitro-group taking place. This indicates clearly that an acetylamino-group exercises much less influence on a methoxy-group when in the para-position with respect to it than when in the ortho. This view was supported by the fact that 4-acetylaminoveratrole gave on nitration an excellent yield of 5-nitro-4-acetylaminoveratrole (VI), no trace of an isomeride being formed.

EXPERIMENTAL.

5-*Amino*-3:4-*dimethoxybenzoic Acid*.

For the preparation of this acid, the following method was found to yield the most satisfactory results (compare Hayduck, *Ber.*, 1903, **36**, 2930). Vanillin (10 grams) was dissolved in ether (200 grams), and a steady stream of oxides of nitrogen (prepared by the action of dilute sulphuric acid on sodium nitrite) was led through the well-cooled solution for two to three hours. After the addition of a little water, the mixture was allowed to remain overnight, when 5-nitrovanillin crystallised out. This was collected, and after washing with a little ether, in which it was only very sparingly soluble, it was found to be pure, melting at 175—176°. The yield was 8 grams.

The methylation of 5-nitrovanillin offered considerable difficulty, and ultimately the following method was adopted. The finely powdered potassium salt (dried at 130°) was suspended in dry toluene, and, after the addition of a slight excess of methyl sulphate, the mixture was heated at 135—140° for two to three hours in an oil-bath, when the scarlet potassium salt was completely decomposed. The toluene was removed by distillation in a current of steam, and the mixture of 5-nitroveratrole and 5-nitrovanillin was collected and triturated with dilute sodium hydroxide solution, when pure 5-nitroveratrole was obtained, the yield being 50 per cent of the theoretical. By oxidation with potassium permanganate in alkaline solution, a quantitative yield of 5-nitro-3:4-dimethoxybenzoic acid was obtained.

The barium salt of the nitro-acid was readily reduced by means of an alkaline solution of ferrous hydroxide in the usual manner. On concentrating the solution of the barium salt of the amino-acid to a small bulk and rendering strongly acid with concentrated hydrochloric acid, the *hydrochloride* separated in a yield of 50 per cent. of the theoretical. The hydrochloride was purified by crystallisation from a mixture of moist acetone and ethyl acetate or by solution in alcohol and precipitation with concentrated hydrochloric acid, when it was obtained in woolly needles decomposing at 235°:

0·1094 gave 0·0694 AgCl. Cl = 15·6.

$C_9H_{11}O_4N,HCl$ requires Cl = 15·2 per cent.

Attempts to prepare a pure specimen of the amino-acid from the hydrochloride were unsuccessful, the amino-acid darkening with extreme readiness on exposure to the air.

The *platinichloride* separated in fine, glistening, yellow needles

which were readily soluble in water. It possessed no definite melting point, but became brown at about 180° and gradually blackened. It was not melted at 270°. For analysis it was dried at 100°:

0·1799 gave 0·0432 Pt. Pt = 24·0.

$(C_9H_{11}O_4N)_2,H_2PtCl_6$ requires Pt = 24·2 per cent.

5-*Acetylamino*-3:4-*dimethoxybenzoic acid* (I), prepared in the usual manner from the hydrochloride, separated from hot water in glistening, fine needles containing one molecule of water of crystallisation, which was lost on drying at 100°. It softened at 117° and melted at 126°, the anhydrous substance melting at 188°:

*0·4385 lost 0·0314 H_2O at 100°. H_2O = 7·2.

†0·1059 gave 0·218 CO_2 and 0·0511 H_2O. C = 55·3; H = 5·4.

$C_{11}H_{13}O_5N,H_2O$ requires H_2O = 7·0 per cent.

$C_{11}H_{13}O_5N$ requires C = 55·2; H = 5·4 per cent.

Nitration of 5-*Acetylamino*-3:4-*dimethoxybenzoic Acid.* 6-*Nitro*-5-*acetylamino*-3:4-*dimethoxybenzoic Acid* (II), *and* 4:5-*Dinitro*-3-*acetylaminoveratrole* (III).

In one experiment, 5-acetylamino-3:4-dimethoxybenzoic acid (2 grams) was gradually added to nitric acid (D 1·52; 6 grams), which was kept well cooled in a mixture of salt and ice. The reaction proceeded with considerable evolution of gas, and after ten minutes the extremely viscid, yellow liquid was poured on ice, when an oil separated which gradually solidified. The solid was collected, washed with a little ice water, and triturated with a dilute solution of sodium carbonate. The insoluble residue (0·9 gram) was crystallised from acetic acid, when it was obtained in glistening needles melting at 241°, and was found to consist of 4:5-dinitro-3-acetylaminoveratrole, identical in every respect with the substance described by Gibson, Simonsen, and Rau (T., 1917, **111**, 78). (Found, N = 15·1. Calc., N = 14·7 per cent.).

The alkaline solution from which the dinitro-compound had been separated was acidified, when the *nitroacetylamino-acid* was precipitated in pale brownish-yellow crystals (1·2 grams). It was purified by crystallisation from dilute alcohol:

0·143 gave 14 c.c. N_2 at 32° and 760 mm. N = 10·3.

$C_{11}H_{12}O_7N_2$ requires N = 9·9 per cent.

6-*Nitro*-5-*acetylamino*-3:4-*dimethoxybenzoic acid* crystallises in straw-coloured needles which decompose at 220—221°. It is readily soluble in alcohol or acetone, very sparingly so in water, benzene, chloroform, or ethyl acetate, but more readily so in hot water.

* Air dried. † Dried at 100°.

When heated on the water-bath with hydrochloric acid (50 per cent.) for some hours, it gradually passed into solution, and on neutralising the excess of mineral acid with ammonia, the *amino*-acid separated as a pale yellow, crystalline powder. It was re-crystallised from a mixture of ethyl acetate and benzene:

0·13 gave 15 c.c. N_2 at 30° and 760 mm. N = 12·4.

$C_9H_{10}O_6N_2$ requires N = 12·2 per cent.

6-*Nitro*-5-*amino*-3 : 4-*dimethoxybenzoic acid* crystallises in iridescent yellow, prismatic needles which melt at 148°.* It is readily soluble in acetone, ethyl acetate, or alcohol, but very sparingly so in water or benzene.

Diazotisation of 6-*Nitro*-5-*amino*-3 : 4-*dimethoxybenzoic Acid.* 6-*Nitro*-3 : 4-*dimethoxybenzoic Acid* (IV).

The amino-acid (0·5 gram) was dissolved in alcohol (5 c.c.), and, after the addition of sulphuric acid (1 gram), amyl nitrite (1 gram) was added to the well-cooled mixture. The clear solution gradually became cloudy, and after some minutes the sparingly soluble diazonium salt crystallised. This was decomposed on the water-bath, and on pouring into water a reddish-yellow solid separated, which was found to be a mixture of 6-nitro-3 : 4-dimethoxybenzoic acid and a phenolic acid. It was therefore dissolved in alkali and methylated with methyl sulphate in the usual manner, treated with potassium permanganate to remove a trace of phenolic acid, and the solution filtered and concentrated, when, on acidifying, the nitro-acid was obtained as a caseous, white precipitate. It was re-crystallised from hot water, when it was obtained in fine needles melting at 185—187°, and this melting point was unaltered on admixture with a specimen of the 6-nitro-acid from another source. As a further proof of the constitution of this acid, the methyl ester was prepared. It crystallised in fine needles melting at 143—144°, which is the melting point of methyl 6-nitro-3 : 4-dimethoxybenzoate.

6-*Acetylamino*-3 : 4-*dimethoxybenzoic Acid* (V).

This substance, which does not seem to have been prepared previously, was readily obtained when the hydrochloride of the amino-acid (*Ber.*, 1876, **9**, 942) was warmed with acetic anhydride. It was crystallised from dilute acetic acid, when it was obtained in colourless, irregular prisms decomposing at 228°:

* On one occasion a trace of an acid was isolated which crystallised in plates and melted at about 180°. It was probably the isomeric nitro-acid but it was not obtained in sufficient quantity for analysis.

0·1857 gave 10·4 c.c. N_2 at 30° and 760 mm. N = 6·0.
$C_{11}H_{13}O_5N$ requires N = 5·9 per cent.

Nitration of 6-Acetylamino-3 : 4-dimethoxybenzoic Acid. 5-Nitro-4-acetylaminoveratrole (VI).

A large number of experiments were made with the view of finding a method for nitrating the amino-acid without the elimination of the carboxyl group, but in this we were unsuccessful. In one experiment, the finely powdered acetylamino-acid (2 grams) was slowly added to nitric acid (D 1·42; 6 grams), well cooled in a mixture of salt and ice. The acid dissolved with the evolution of gas, and in a short time the whole mass became pasty owing to the separation of the nitro-derivative. After fifteen minutes, the mixture was poured on ice, and the yellow solid collected (2 grams). It was found to be quite homogeneous, and was purified by crystallisation from alcohol:

0·1061 gave 11·8 c.c. N_2 at 30° and 759 mm. N = 11·9.
$C_{10}H_{12}O_5N_2$ requires N = 11·7 per cent.

5-*Nitro-4-acetylaminoveratrole* separates from alcohol in golden-yellow needles melting at 196°. It is insoluble in water, sparingly soluble in cold alcohol or acetic acid, but more readily so in hot alcohol or acetic acid.

5-*Nitro-4-aminoveratrole*.—This substance was readily obtained when the foregoing compound was dissolved in sulphuric acid (90 per cent.) and the solution heated at 100° for ten minutes. On pouring into water, the *nitroamine* separated as a yellow powder, and was purified by crystallisation from alcohol:

0·1054 gave 14 c.c. N_2 at 30° and 759 mm. N = 14·3.
$C_8H_{10}O_4N_2$ requires N = 14·1 per cent.

5-*Nitro-4-aminoveratrole* crystallises in terra-cotta-coloured needles melting at 171°. It is readily soluble in acetone, hot alcohol, or hot ethyl acetate, but very sparingly so in benzene or chloroform. It dissolves readily in concentrated mineral acids, but is reprecipitated on dilution. The high melting point of this nitroamine is somewhat remarkable, and in order to make certain that no change had taken place on hydrolysis, it was treated with acetic anhydride, when the acetyl derivative melting at 196° was obtained.

The benzoyl derivative crystallised from alcohol in sulphur-yellow, woolly needles melting at 153—154°.

When diazotised with amyl nitrite in alcoholic solution in the usual manner, the nitroamine gave a nearly quantitative yield of 4-nitroveratrole melting at 95—96°. (Found, N = 7·6. Calc.,

N=7·6 per cent.) There can therefore be no doubt as to its constitution.

4-Aminoveratrole.

The preparation of 4-aminoveratrole by the reduction of 4-nitroveratrole offered some difficulty owing to the tendency for chlorination to take place simultaneously. Ultimately, the following method was found to give fairly satisfactory results. 4-Nitroveratrole (10 grams) was mixed with tin (16 grams), and, after the addition of a trace of graphite (compare Pinnow, *J. pr. Chem.*, 1901, [ii], **63**, 352), hydrochloric acid (50 c.c. of 50 per cent.) was added, and the mixture heated on the water-bath for from two to three hours. The yield of 4-aminoveratrole, isolated in the usual manner, was about 50 per cent. of the theoretical.

Nitration of 4-Acetylaminoveratrole.

To nitric acid (D 1·4; 6 grams), well cooled in a mixture of salt and ice, finely powdered 4-acetylaminoveratrole [VII] (2 grams) was gradually added. The nitration proceeded with considerable evolution of gas, and in a short time the whole mass became pasty. After fifteen minutes, the mixture was poured on ice, when a yellow solid separated. This was collected, and found to melt at 195° (1·4 grams). It was crystallised from alcohol, when it was obtained in golden-yellow needles melting at 196°, and was found to be identical in every respect with the 5-nitro-4-acetylaminoveratrole obtained by the nitration of 6-acetylamino-3:4-dimethoxybenzoic acid (see above):

0·0727 gave 0·1337 CO_2 and 0·0352 H_2O. C=50·1; H=5·3.

$C_{10}H_{12}O_5N_2$ requires C=50·0; H=5·0 per cent.

THE PRESIDENCY COLLEGE,
MADRAS.

[*Received, November 6th,* 1917.]

V.—*Studies in Phototropy and Thermotropy. Part VIII. Cinnamylideneamines. 2:4-Dihydroxybenzylideneamines.*

By ALFRED SENIER and PATRICK HUGH GALLAGHER.

THIS communication is a report of further study of the condensation products of aromatic aldehydes with amines, the anils, or Schiff's bases, with a view to the discovery and special examination of such as might exhibit phototropic or thermotropic change.

Previous communications have shown that whilst compounds of this class are generally thermotropic, they are not phototropic unless they contain an hydroxyl group in an ortho-position with respect to the aldehyde group of the benzylidene nucleus. Moreover, the property appears to be inhibited by the entry into the nucleus of such substituents as bromine, methyl, or methoxyl.

With one possible exception (Foresti, *Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 270), phototropy has not been observed except in the case of solids, and it has been suggested (Senier and Shepheard, T., 1909, **95**, 1944) that it is not due to intramolecular change, but to reversible extra-molecular rearrangement of the molecules into molecular aggregates. In order to determine, if possible, whether this explanation or some other is the true one, we are endeavouring to discover further instances of phototropic compounds for study.

We wished to examine the 2-hydroxycinnamylideneamines, but practical difficulties at the present time have prevented us. This paper contains, however, an account of the preparation and investigation of the simpler cinnamylideneamines, and also of 2:4-dihydroxybenzylideneamines, which latter contain, in addition to an *o*-hydroxyl group, another hydroxyl group in the *p*-position.

None of the compounds is phototropic between "the lower temperature," that of solid carbon dioxide, and "the higher temperature," just below their melting points. Prolonged exposure to actinic light, however, induces permanent *polymorphic* change in many instances. Thermotropy was detected in nearly all cases. Differences of colour in solution depending on the solvent employed were generally observed. The solutions in acetic acid or chloroform were usually deeper in colour than those in light petroleum, benzene, or acetone (compare Senier and Shepheard, T., 1909, **95**, 1943). Trituration appears to yield a *polymorphic variety* in the case of cinnamylidene-*m*-bromoaniline, but was not otherwise observed. No tritoluminescence was detected.

The 2:4-dihydroxybenzylidene derivatives exhibit marked *dichroism* in solution. They are green in very thin layers or in dilute, and yellow in thicker layers or when the solutions are concentrated. The green colour of thin layers appears to partake of the character of fluorescence, for it persists when viewed with light from a blue or violet light-filter.

Most of the compounds are readily formed by mixing alcoholic solutions of the aldehyde and base. The ortho-substituted anilines, however, combine with the aldehydes only on prolonged heating at 100°. Attempts to prepare mono-derivatives of phenylene- and naphthylene-diamines resulted in the formation of di-derivatives.

The source of actinic light employed was direct sunlight or a mercury lamp. The compounds dissolve generally in the usual organic solvents; any important exception is noted.

Cinnamylideneaniline, $C_6H_5\cdot CH:CH\cdot CH:N\cdot C_6H_5$ (Döbner and Miller, *Ber.*, 1883, **16**, 1665), consists of yellow plates which melt at 109° (corr.). It is changed into a deeper coloured *polymorphic form* by the prolonged action of actinic light, and is thermotropic at both "the higher" and "the lower temperatures."

Cinnamylidenechloroanilines, $C_6H_5\cdot CH:CH\cdot CH:N\cdot C_6H_4Cl$.

Cinnamylidene-o-*chloroaniline* at first separates mixed with tarry matter, which may be removed by careful washing with alcohol, light petroleum, or ether. After several crystallisations, it becomes nearly colourless, the crystals showing a pale greenish-yellow tinge. It melts at 63·5° (corr.):

0·1324 gave 7 c.c. N_2 at 17° and 767 mm. N=5·96.
$C_{15}H_{12}NCl$ requires N=5·80 per cent.

This compound shows no change of colour by the action of actinic light or by changes of temperature.

Cinnamylidene-*p*-chloroaniline (James and Judd, T., 1914, **105**, 1430) crystallises in pale yellow or, as in our experiment, in nearly colourless plates which melt at 107° (corr.). It is not phototropic, but exhibits thermotropy at "the higher," and in a less degree at "the lower temperatures."

Cinnamylidenebromoanilines, $C_6H_5\cdot CH:CH\cdot CH:N\cdot C_6H_4Br$.

Cinnamylidene-o-*bromoaniline* separates from alcoholic solution in pale greenish-yellow clusters which melt at 74° (corr.):

0·1668 gave 7·1 c.c. N_2 at 19° and 762 mm. N=4·98.
$C_{15}H_{13}NBr$ requires N=4·88 per cent.

Slight thermotropy was detected both above and below the ordinary temperature.

Cinnamylidene-*m*-bromoaniline (James and Judd, T., 1914, **105**, 1434) consists of pale yellow plates which melt at 122° (corr.). (The above authors found 115—116°.) Prolonged action of actinic light produces a slight permanent deepening of colour, and slight evidence of thermotropy was observed.

Cinnamylidene-p-*bromoaniline* crystallises from alcohol, chloroform, or benzene in pale greenish-yellow plates which melt at 120° (corr.). A permanent deepening in colour occurs when this com-

pound is submitted to the prolonged action of actinic light, and thermotropy was observed at "the lower temperature."

0·1402 gave 5·9 c.c. N_2 at 16° and 768 mm. N=4·885.

$C_{15}H_{13}NBr$ requires N=4·88 per cent.

Cinnamylidenetoluidines, $C_6H_5·CH:CH·CH:N·C_6H_4Me$.

Cinnamylidene-*o*-toluidine (James and Judd, T., 1914, **105**, 1433), which melts at 73°, is not affected by actinic light or by temperature changes under its melting point.

Cinnamylidene-*m*-toluidine is neither phototropic nor thermotropic (Senier and Shepheard, T., 1909, **95**, 1955).

Cinnamylidene-*p*-toluidine (Tinkler, T., 1913, **103**, 894) consists of pale greenish-yellow plates which melt at 83° (corr.). Slight deepening of colour occurred by the prolonged action of actinic light. No evidence of thermotropy was observed.

Cinnamylidenenitrotoluidines, $C_6H_5·CH:CH·CH:N·C_6H_3Me·NO_2$.

*Cinnamylidene-4-nitro-*o*-toluidine* forms pale greenish-yellow clusters which melt at 126° (corr.):

0·1140 gave 10·4 c.c. N_2 at 19° and 757 mm. N=10·54.

$C_{16}H_{15}O_2N_2$ requires N=10·50 per cent.

This compound forms deeper coloured solutions in alcohol or acetic acid than in the other ordinary solvents. It is not phototropic, but is thermotropic at "the higher temperature."

*Cinnamylidene-2-nitro-*p*-toluidine* crystallises from alcohol in pale yellow leaflets which melt at 108° (corr.):

0·2388 gave 21·2 c.c. N_2 at 15° and 767 mm. N=10·58.

$C_{16}H_{15}O_2N_2$ requires N=10·50 per cent.

This compound is not affected by actinic light, but exhibits thermotropy at both "the higher" and "the lower temperatures."

Cinnamylidene-*m*-nitroaniline (James and Judd, 1914, **105**, 1434) is not thermotropic, nor is it affected by actinic light.

*Cinnamylidene-*p*-anisidine*, $C_6H_5·CH:CH·CH:N·C_6H_4·OMe$, is obtained from solutions in alcohol in large yellow plates which melt at 119° (corr.):

0·1106 gave 5·6 c.c. N_2 at 16° and 759 mm. N=6·00.

$C_{16}H_{15}ON$ requires N=5·93 per cent.

This base dissolves sparingly in cold alcohol. Acetic acid changes the yellow crystals into a scarlet, probably *dimorphic variety*, which we propose to examine further. It is not affected

by actinic light, but is slightly thermotropic at "the lower temperature."

Cinnamylidene-p-*phenetidine*, $C_6H_5\cdot CH\colon CH\cdot CH\colon N\cdot C_6H_4\cdot OEt$, consists of pale green, lustrous plates which melt at 108° (corr.). Like the preceding base, acetic acid changes it into a red *dimorphic variety*, which crystallises in prisms. It is slightly thermotropic, but is not phototropic:

0·1328 gave 6·2 c.c. N_2 at 15° and 767 mm. N = 5·58.
$C_{17}H_{17}ON$ requires N = 5·58 per cent.

Cinnamylidene-p-*xylidine*, $C_6H_5\cdot CH\colon CH\cdot CH\colon N\cdot C_6H_3Me_2$, separates in pale yellow needles which melt at 111·5° (corr.):

0·0856 gave 4·3 c.c. N_2 at 15° and 764 mm. N = 6·08.
$C_{17}H_{17}N$ requires N = 5·95 per cent.

This compound is not affected by actinic light, but exhibits slight thermotropy at both "the higher" and "the lower temperatures."

Cinnamylidene-ψ-cumidine, $C_6H_5\cdot CH\colon CH\cdot CH\colon C_6H_2Me_3$ (Schiff, *Annalen*, 1887, **239**, 384), which melts at 105°, is not affected by actinic light, but is thermotropic at both "the higher" and "the lower temperatures."

Cinnamylidenenitro-ψ-cumidine,

$$C_6H_5\cdot CH\colon CH\cdot CH\colon N\cdot C_6HMe_3\cdot NO_2$$

—This base separates at first in orange-red needles. After several recrystallisations, yellow crystals are obtained, which revert to orange-red on keeping. After further recrystallisations, however, the product retains its yellow colour. It melts at 117° (corr.). Actinic light has no effect on this base, nor is it thermotropic:

0·2424 gave 20 c.c. N_2 at 17° and 759 mm. N = 9·63.
$C_{18}H_{18}O_2N_2$ requires N = 9·53 per cent.

Cinnamylidene-β-naphthylamine, $C_6H_5\cdot CH\colon CH\cdot CH\colon N\cdot C_{10}H_7$ (Schiff, *Annalen*, 1887, **239**, 384), is stated to melt at 95—96°. Our specimen melts at 124° (corr.). (Found, N = 5·41. $C_{19}H_{15}N$ requires N = 5·46 per cent.)

This base is neither phototropic nor thermotropic, but by the prolonged action of actinic light it changes into a deeper coloured *polymorphic form*.

Cinnamylidenecamphylamine was prepared, but as it proved to be a liquid and the quantity was small, we did not proceed with it further.

Dicinnamylidene-p-*phenylenediamine*,

$$(C_6H_5\cdot CH\colon CH\cdot CH\colon N)_2C_6H_4,$$

separates from alcohol as a pale yellow powder which melts at 209° (corr.). It is not phototropic or thermotropic:

0·1802 gave 12·6 c.c. N_2 at 17° and 760 mm. N=8·04.
$C_{24}H_{20}N_2$ requires N=8·34 per cent.

Dicinnamylidene-o-naphthylenediamine,
$(C_6H_5\cdot CH:CH\cdot CH:N)_2C_{10}H_6$,
separates readily in brick-red crystals, but on being left in contact with the solvent, they change into a viscous, red tar. By quickly recrystallising several times from alcohol, and subsequently washing with ether and drying, the compound melts at 136° (corr.):

0·1364 gave 8·7 c.c. N_2 at 21° and 766 mm. N=7·66.
$C_{26}H_{22}N_2$ requires N=7·74 per cent.

This compound dissolves in the usual organic solvents, giving blood-red solutions; the solutions in ethyl, methyl, or amyl alcohols, and in ether, ethyl acetate, or acetone, exhibit a strong blue fluorescence; those in toluene or xylene are slightly fluorescent; those in benzene or nitrobenzene are not fluorescent. On keeping, even in the dry state, this base changes into a *dimorphic variety* of a yellowish-grey colour which melts at 112° (corr.). When dissolved, this modification appears to revert to the original compound.

Dicinnamylidenebenzidine, $(C_6H_5\cdot CH:CH\cdot CH:N\cdot C_6H_4)_2$ (Schiff, *Annalen*, 1887, **239**, 385), is obtained easily as a yellow powder. It melts at 249° (corr.). Acetic acid dissolves it, forming a red solution, but it is only sparingly soluble in the other organic solvents. It is thermotropic at "the higher temperature," but is not affected by actinic light:

0·1098 gave 6·4 N_2 at 16° and 768 mm. N=6·92.
$C_{30}H_{24}N_2$ requires N=6·80 per cent.

2:4-*Dihydroxybenzylideneaniline*, $(OH)_2C_6H_3\cdot CH:N\cdot C_6H_5$, forms pale greenish-yellow needles from solution in most organic solvents. It melts at 99·5° (corr.) (Dimroth and Zoeppritz, *Ber.*, 1902, **35**, 995, give 125—126°, and Gattermann, *Annalen*, 1907, **357**, 336, gives 131°). (Found, N=6·39. $C_{13}H_{11}O_2N$ requires N=6·57 per cent.)

This compound is thermotropic, both at the higher and the lower temperatures; it is not phototropic, but changes into a deeper coloured *polymorphic form* on prolonged exposure to actinic light.

2:4-*Dihydroxybenzylidene-o-bromoaniline*,
$(OH)_2C_6H_3\cdot CH:N\cdot C_6H_4Br$.
—The product consisted of a reddish-yellow tar, which eventually solidified, and yielded by treatment with solvents a reddish-yellow,

amorphous powder; this separated from benzene solution in crystals melting at 91° (corr.):

0·1210 gave 5·0 c.c. N_2 at 22° and 762 mm. N=4·68.
$C_{13}H_{10}O_2NBr$ requires N=4·79 per cent.

This compound is thermotropic both at "the higher" and "the lower temperatures," and yields a *polymorphic form* by long exposure to actinic light, but is not phototropic.

2:4-*Dihydroxybenzylidene*-m-*bromoaniline*.—The first product of the reaction is a deep red liquid which soon solidifies. The substance separates from benzene solution in deep yellow crystals melting at 111·5° (corr.):

0·2829 gave 11·8 c.c. N_2 at 15° and 751 mm. N=4·86.
$C_{13}H_{10}O_2NBr$ requires N=4·79 per cent.

The yellow crystals are changed into a red *dimorphic form* by contact with acetic acid or benzene, and an orange-coloured product was noticed on prolonged exposure to actinic light and also on trituration. It is not phototropic, but exhibits thermotropy at "the lower temperature."

2:4-*Dihydroxybenzylidene*-p-*bromoaniline* crystallises in pale greenish-yellow needles from alcohol, chloroform, or acetone, or in plates from acetic acid or benzene. It melts at 124° (corr.):

0·1840 gave 7·6 c.c. N_2 at 16° and 751 mm. N=4·78.
$C_{13}H_{10}O_2NBr$ requires N=4·79.

This base is not phototropic, but changes to a deeper coloured *polymorphic form* on long exposure to actinic light. It is thermotropic at both "the higher" and "the lower temperatures."

2:4-*Dihydroxybenzylidene*-m-*toluidine*,

$$(OH)_2C_6H_3{\cdot}CH{:}N{\cdot}C_6H_4Me.$$

—The first product of the reaction consisted of a mass of scarlet crusts and yellow needles (*dimorphic forms*). On recrystallisation, the whole separated in yellow needles, which melt at 137° (corr.):

0·0976 gave 5·1 c.c. N_2 at 20° and 762 mm. N=6·05.
$C_{14}H_{13}O_2N$ requires N=6·17 per cent.

This compound is thermotropic both at "the higher" and "the lower temperatures"; it is not phototropic, but acted on by actinic light yields a deeper coloured *polymorphic form*.

2:4-*Dihydroxybenzylidene-β-naphthylamine*,

$$(OH)_2C_6H_3{\cdot}CH{:}N{\cdot}C_{10}H_7,$$

separates from acetone in yellow needles or from alcohol in yellow plates. It melts at 160·5° (corr.):

0·1220 gave 5·6 c.c. N_2 at 20° and 762 mm. N=5·31.
$C_{17}H_{13}O_2N$ requires N=5·32 per cent.

This compound is not affected by actinic light, but is thermotropic at the higher temperature, changing to an orange thermotrope.

2:4-*Dihydroxybenzylidenecamphylamine*,

$$(OH)_2C_6H_3\cdot CH:N\cdot CH_2\cdot C_9H_{15}.$$

—Pale greenish-yellow needles of this compound separate from solutions in alcohol, chloroform, benzene, or acetone. These melt at 133° (corr.). In acetic acid it dissolves, forming a colourless solution—a *dimorphic form*—but from this solution we were only able to obtain a small quantity of a yellow oil. The yellow needles are not phototropic, but are slightly thermotropic both at "the higher" and at "the lower temperatures":

0·1537 gave 7 c.c. N_2 at 15° and 768 mm. N=5·04.

$C_{17}H_{23}O_2N$ requires N=5·13 per cent.

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[*Received, December 3rd*, 1917.]

VI.—*Studies on the Sulphonation of β-Naphthylamine.*

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THE isomeric β-naphthylaminesulphonic acids are of considerable importance in the dye industry partly as such and partly for the preparation of other intermediate compounds. It therefore appeared to be of interest to submit the sulphonation of β-naphthylamine to a more detailed study than has yet been published, directed to ascertaining the mechanism of the reactions involved, the circumstances favouring the production of the respective isomerides, and the conditions for the conversion of one into another.

Previous workers have shown (Badische Anilin- & Soda-Fabrik, D.R.-P., 20760; Dahl & Co., E.P., 7712 of 1884; Bayer and Duisberg, *Ber.*, 1887, **20**, 1426; Forsling, *Ber.*, 1886, **19**, 1815; 1887, **20**, 2103; Green, T., 1889, **55**, 33) that the sulphonation of β-naphthylamine gives rise to four monosulphonic acids, originally distinguished by the prefixes α, β, γ, and δ, to which, principally through the researches of Armstrong and Wynne (P., 1888, **4**, 105; 1889, **5**, 48; 1890, **6**, 128), the respective constitutions 2:8, 2:6, 2:5, and 2:7 have been assigned. Of these isomeric acids, those containing the sulphonic group in an α-position, namely, the 2:8 and the 2:5 acids, are simultaneously formed by sulphonation at low temperatures (15° to 100°), whilst those containing

the sulphonic group in a β-position, namely, the 2:6- and the 2:7-acids, are formed simultaneously by sulphonation at high temperatures (150° and above). The two homonucleal sulphonic acids, 2:1 and 2:4, have so far not been obtained by the sulphonation of β-naphthylamine, but are prepared by the action of ammonia on the corresponding sulphonic acids of β-naphthol.

EXPERIMENTAL.

The sulphonations were carried out under exactly comparable conditions, using a wide-mouthed, round-bottomed flask of 300 c.c. capacity closed by a rubber stopper, through which passed a glass tube terminating in a fine orifice in order to exclude the entrance of moisture during the operation. Ten grams of pure β-naphthylamine (twice distilled, m. p. 112°) were used for each sulphonation. This was coarsely powdered so as to pass a 30-mesh sieve, and added during ten minutes to the sulphuric acid contained in the flask, which was constantly shaken. The quantity of sulphuric acid used was four parts (40 grams) of 96 or 100 per cent. acid, or three parts (30 grams) of fuming sulphuric acid containing 20 per cent. of sulphur trioxide. As solution occurs, the temperature rises to nearly 60°, and if sulphonation below this temperature is desired, the flask must be cooled from time to time. As soon as solution was effected, the flask was stoppered and immersed in an oil-bath, the temperature of which was carefully regulated, where it was maintained at the requisite temperature for the time specified. The product was then mixed with 100 c.c. of water, and any lumps that were formed were broken down with a pestle. After half an hour, the precipitated sulphonic acid was collected on a Büchner funnel and washed with 75 c.c. of cold water, care being taken to keep the surface unbroken. The precipitate was then transferred to a porcelain dish, mixed to a fine paste with 50 c.c. of water, the mixture being heated to boiling and neutralised with $2N$-sodium hydroxide, using phenolphthalein as indicator. The quantity of sodium hydroxide required for neutralisation indicates whether the sulphonation has proceeded correctly and whether the product has been washed free from sulphuric acid. If an incorrect quantity was used, the experiment was rejected. After cooling (and filtering to remove any β-naphthylamine if present), the solution of the sodium salt was evaporated to dryness on the water-bath, dried sharply at 100—105°, and weighed. In nearly every case the yield was about 96 per cent. of the theoretical.

For the separation and estimation of the isomeric acids, use was made, in the first place, of the insolubility of the sodium salt of

the 2:8-isomeride in 90—94 per cent. alcohol (Dahl's method). The sodium salts entering into solution consist of the 2:5-isomeride, together with any 2:6- and 2:7-isomerides that may be present in the sulphonation mixture. For the separation of the former from the two latter, a satisfactory method, based on the different solubility of the silver salts, was discovered. Whereas the silver salt of the 2:5-acid is fairly soluble in water, the silver salts of the 2:6- and 2:7-acids are very sparingly soluble and separate as white, silky precipitates on adding silver nitrate to even dilute solutions of the sodium salts.

In carrying out these separations, the dry sodium salt, obtained as above, was well powdered and a weighed quantity (15—16 grams) was extracted three times in succession with boiling 92—94 per cent. alcohol, using at each extraction about 90 grams of alcohol and boiling for fifteen to twenty minutes. The filtrates were united, the alcohol was distilled off, and the soluble and insoluble sodium salts were weighed after being dried. The latter consisted of practically pure 2:8-sulphonate, whilst the former was free from this salt, but contained the remaining isomerides. For the estimation of the 2:6- and 2:7-acids, 1 gram of the alcohol-soluble salt is dissolved in 20 c.c. of water in a small conical flask provided with a rubber stopper. Silver nitrate (5 to 10 c.c. of $N/5$-solution) is added, the mixture well shaken, and the precipitate collected after remaining for three or four minutes. The precipitated silver salt is washed with cold water and dissolved from the filter by ammonia. The solution is diluted to 100—200 c.c., boiled, and acidified with hydrochloric acid. The silver chloride is collected on a tared filter-paper, washed with boiling water, and weighed. From the weight of silver chloride obtained, the percentage of 2:6- and 2:7-acids is calculated, the difference being the 2:5-acid. The hot filtrate on cooling deposits the 2:6- and 2:7-acids in glistening plates. The accuracy of the method was demonstrated on mixtures containing known proportions of the respective isomerides.

The following numbers represent in nearly all cases the results of at least two concordant experiments.

Effect of Temperature.

In this series of experiments, sulphonation was effected with four parts of 96 per cent. sulphuric acid for five hours, whilst the temperature was raised from 40° to 120°.

No. of experiment.	Temperature.	Percentage of isomeric acids in product. 2 : 8.	2 : 5.	2 : 6 and 2 : 7.
1	40°	38	61·6	0·4
2	60	36	63·5	—
3	80	44	55·3	0·7
4	90	42	57·3	—
5	100	41	58·3	0·7
6	120	26	66·5	7·5

In experiments 2 and 4, the amount of 2:6- and 2:7-acids was not determined, but an average value was assumed in arriving at the percentage of the 2:5-acid.

It is seen that the maximum yield of the 2:8-acid is obtained at about 80° and diminishes with increase of temperature above this limit, whilst it is also somewhat less at lower temperatures.

Effect of Time.

The sulphonation was effected at 80°, using the same proportion of 96 per cent. sulphuric acid as in the previous series, but the time of reaction was varied from ten minutes to twenty-five hours.

No. of experiment.	Time, in hours.	Percentage of isomeric acids in product. 2 : 8.	2 : 5.	2 : 6 and 2 : 7.
7	1	42	57·3	0·7
8	2½	43	56·3	—
9	5	44	55·3	0·7
10	10	43	55·1	1·9
11	15	37	61·0	—
12	20	36	61·6	2·4
13	25	35	62·0	—

In experiments 8, 11, and 13, the amount of 2:6- and 2:7-acids was not determined, but an assumed value was used in arriving at the percentage of the 2:5-acid. The sulphonation is just completed within one hour, a shorter time than this leaving a little unaltered β-naphthylamine.

In order to ascertain the effect of reducing the time of reaction to the lowest possible limit, the following sulphonation was effected in about fifteen minutes at 50—60°. About 10 per cent. of the β-naphthylamine remained unsulphonated, and was collected after dissolving the acid in sodium carbonate solution.

No. of experiment.	Time and temperature.	Percentage of isomeric acids in product. 2 : 8.	2 : 5.	2 : 6 and 2 : 7.
14	15 minutes at 50–60°.	28	71·2	0·8

Effect of Strength of Sulphuric Acid.

In order to determine the effect of the concentration of the acid, sulphonations were conducted at varying temperatures with 92, 96 (results already given), and 100 per cent. sulphuric acid, and also with fuming sulphuric acid containing 20 per cent. of sulphur trioxide. With one exception, the time of reaction was fixed at five hours. In the experiment marked with an asterisk it was only ten to fifteen minutes. The following table gives the percentages of 2:8-acid found. When 92 per cent. sulphuric acid was employed, about 10 per cent. of β-naphthylamine escaped sulphonation.

	Acid strength.			
Temperature of sulphonation.	92 per cent. H_2SO_4.	96 per cent. H_2SO_4.	100 per cent. H_2SO_4.	20 per cent. SO_3.
20°	—	—	33	—
40°	—	38	39	38*
60°	—	36	38	—
80°	40°	44	40	46
90°	—	42	—	—
100°	—	41	23	—
120°	—	26	32	—

The percentage of 2:6- and 2:7-isomerides was only determined in the alcohol-soluble sodium salts obtained from the series of sulphonations made at 80°:

With	92 per cent.	H_2SO_4	0·9	per cent. of 2 : 6- and 2 : 7-acids.
,,	96 ,,	H_2SO_4	0·7	,, ,, ,,
,,	100 ,,	H_2SO_4	1·5	,, ,, ,,
,,	20 ,,	SO_3	2·7	,, ,, ,,

Conclusions from above Results.

It would appear from the results obtained that within temperatures ranging from 20° to 80° there is only a small variation in the proportion of the 2:8- to the 2:5-isomeride, which together constitute 97—99·5 per cent. of the entire sulphonation product.

The effect of variations in time is very similar; for periods between one hour and ten hours there is little difference in the proportion of the isomerides formed. Also within these limits of temperature and time the strength of the sulphuric acid appears to exert but little influence, with the exception that at 80° a small rise in the amount of the 2:6- and 2:7-isomerides is noticeable, with an increase in the concentration of sulphur trioxide.

Although within the limits of time and temperature mentioned the proportion of 2:8- and 2:5-acids does not greatly vary, the

lowest temperatures and shortest time of reaction seem to favour the production of the 2:5-acid.

Above the limits of time and temperature defined, a more marked variation becomes apparent, the time and temperature at which this change sets in being somewhat lowered as the concentration of acid is increased. In proportion as the temperature of 80° is exceeded or the sulphonation period (at 80°) is prolonged beyond ten hours, the percentage of the 2:8-acid falls, whilst that of the 2:5-acid rises. Simultaneously therewith there is an increased production of the 2:6- and 2:7-acids, the quantity of which reaches 7·5 per cent. with 96 per cent. sulphuric acid at 120°.

This curious result can only be explained in the following way:

The proportion of the 2:8-acid existent at any particular time and temperature may be regarded as a combination of two factors, namely, (*a*) the proportion of the 2:8- and 2:5-isomerides formed simultaneously in the first instance, and (*b*) the amount of subsequent conversion of the 2:8- into the 2:5-acid. Whilst in regard to the first factor low temperature and quick reaction would seem to favour the formation of the 2:5-acid, with regard to the second factor it would appear that the isomeric change of the 2:8- into the 2:5-acid only comes into evidence at temperatures above 80° and for periods of heating (at 80°) more than ten hours. In other words, it may be assumed that for temperatures below 80° the proportion of the 2:8- and 2:5-isomerides is a fixed one for a particular temperature, the sulphonic group entering simultaneously in the 5- and 8-positions. The proportion so fixed is fairly stable and can only be disturbed by heating to temperatures above 80°, by prolonged action of sulphuric acid, or by the use of a higher concentration of sulphur trioxide. The sulphonic group then commences to wander from the 8-position to the 5-position.

Experiments on Isomerisation.

In order to test the validity of the foregoing hypothesis, the behaviour of pure 2:1-, 2:8-, and 2:5-acids towards sulphuric acid was studied under the conditions existent during sulphonation.

Isomerisation of the 2:1-*Acid*.—It has been suggested that the first stage in the sulphonation of β-naphthylamine may be the entry of the sulphonic group in the 1-position, to be quickly followed by a transposition to the 5- and 8-positions. We have not been able in any instance to detect the presence of the 2:1-acid, even when the sulphonation had been conducted at the lowest possible temperature and in the shortest time.* If, therefore, the 2:1-acid is an

* Following a suggestion by Mr. G. Lodge, we have employed for the detection of the 2:1-acid the delicate reaction with bromine water in the

intermediate product, it must undergo isomerisation with great rapidity. In order to test this point, the following experiments were carried out.

A.—A quantity (17 grams) of the pure sodium salt of β-naphthylamine-1-sulphonic acid equivalent to 10 grams of β-naphthylamine was heated with 40 grams of sulphuric acid (96 per cent.) for five hours at 80°. Disappearance of the 2:1-acid only took place slowly. The product was worked up in the usual manner, the resultant dry sodium salt weighing 17 grams. On extraction with alcohol as usual, 46 per cent. of the 2:8-acid was obtained, whilst the portion soluble in alcohol consisted of 52·5 per cent. of the 2:5- and 1·5 per cent. of the 2:6- and 2:7-acids.

B.—Another experiment was performed under the same conditions, but with 100 per cent. sulphuric acid. The change of the 2:1-acid again occurred very slowly, and it was possible to detect it by the bromine test even after three hours' heating. After five hours the transformation was complete, and the product was then found to contain 40 per cent. of the 2:8-acid.

C.—In a third experiment, made with 96 per cent. sulphuric acid, the mixture was heated only for ten or fifteen minutes to 50—60°. In this case, 8 per cent. of β-naphthylamine was obtained, whilst the greater part of the product was unchanged 2:1-acid.

From the formation of β-naphthylamine in experiment *C*, and the production of the isomeric acids in experiments *A* and *B* in the same proportion as they are obtained by the direct sulphonation of β-naphthylamine, it may be inferred that the isomerisation is brought about by hydrolysis of the 2:1-acid to β-naphthylamine and subsequent resulphonation. In view of the considerable stability of the 2:1-acid under the conditions of sulphonation, it is clear that this acid cannot be an intermediate stage of the direct sulphonation. Hence in the latter, the sulphonic group must enter the second nucleus directly and not through intermediate formation of the homonucleal isomeride.

Isomerisation of the 2:8-Acid.—The pure 2:8-acid was heated with sulphuric acid (96 per cent.) at 80° for five hours. On working up the product as usual, it was found that 32 per cent. in one case and 27 per cent. in another had been converted into the 2:5-isomeride. The rate of this transformation under different

cold by which 1-bromo-β-naphthylamine is formed with the elimination of sulphuric acid. This reaction may also be used for the quantitative estimation of the 2:1-acid by weighing the sulphuric acid eliminated as barium sulphate. All other monosulphonic acids of β-naphthylamine give brominated acids without elimination of the sulphonic group (compare Vaubel, *Zeitsch. angew. Chem.*, 1900, **14**, 686).

conditions is shown in the following series of experiments, in which the pure sodium salt of the 2:8-acid (10 grams) was heated with sulphuric acid (80 grams) at varying temperatures and concentrations for a period of ten hours.

	Temperature.	2:8-Acid unconverted.	2:5-Acid formed (containing less than 1 per cent. of 2:6 and 2:7).
	80°	78·5	21·5
With 80 per cent. H_2SO_4	90	72·8	27·2
	100	70·7	29·3
	110	71·3	28·7
	120	69·8	30·2
With 90 per cent. H_2SO_4	90	63·7	36·3
	100	62·3	37·7
	110	57·2	42·8
	120	56·3	43·7

Isomerisation of the 2:5-*Acid*.—In a similar series of experiments, the pure 2:5-acid was subjected to the action of 96 per cent. sulphuric acid for five hours at 80°. When worked up as usual, the product gave a sodium salt completely soluble in alcohol and containing no 2:8-acid. It consisted almost entirely of unaltered 2:5-acid with a very small percentage of the 2:6- and 2:7-isomerides.

There is therefore no equilibrium established between the 2:8- and 2:5-acids in a sulphuric acid solution, for the isomeric change occurs in one direction only, namely, from 2:8 to 2:5.

Relative Rate of Hydrolysis of the Isomeric Sulphonic Acids.

Whilst the sulphonic group in β-naphthylamine-1-sulphonic acid is somewhat readily removed, the heteronucleal acids are more resistant, although no data are available as to the relative facility with which the different isomerides undergo hydrolysis. It appeared probable that in such differences might be found an explanation of the above facts.

With this object in view, 2 grams of the pure sodium salt of the 2:8-acid was heated with 20 grams of sulphuric acid (60 per cent.) in a small weighed flask on a sand-bath. The water was allowed to evaporate slowly, whilst from time to time samples were withdrawn and tested for β-naphthylamine by neutralisation with sodium hydroxide. No hydrolysis occurred until the temperature reached 145°. At this point, which was found to correspond with a concentration of 70 per cent. sulphuric acid, the undissolved sulphonic acid passed into solution, and at the same time β-naphthylamine was formed.

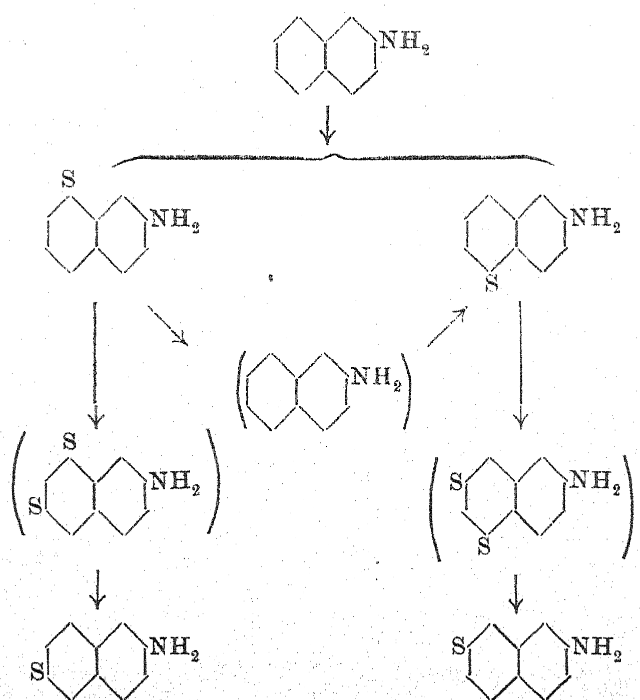
In a similar experiment with the 2:5-acid, solution and hydrolysis did not occur until a temperature of 160° was reached, corresponding with a concentration of 75 per cent. sulphuric acid.

With the 2:6- and 2:7-acids, no evidence of hydrolysis could be obtained even at 175°. The relative facility with which the isomeric acids undergo hydrolysis to β-naphthylamine may therefore be expressed thus:

$$2:1 > 2:8 > 2:5 > 2:6 \text{ and } 2:7.$$

It may therefore be concluded that the gradual conversion of the 2:8- into the 2:5-acid during long heating with sulphuric acid at temperatures of 80° to 120° is brought about by repeated hydrolysis of the 2:8-acid and resulphonation of the β-naphthylamine produced. At each resulphonation, about 40 per cent. of 2:8- and 60 per cent. of 2:5-acid is produced, the former of which is again hydrolysed to β-naphthylamine, and so on.

Simultaneously with the conversion of the 2:8-acid into the 2:5-acid, there also occurs to a less extent a transformation into the 2:6- and 2:7-acids. The last change, which is negligible below 100—110°, becomes considerable at temperatures above 120° (especially when sulphuric acid of high concentration is employed),



until at 150—160° the 2:6- and 2:7-isomerides constitute the main product of sulphonation. It appears probable that the formation of the latter acids is due to concurrent disulphonation and hydrolysis, in which sase the 2:6-acid would originate from the 2:8- and the 2:7-acid from the 2:5.

The entire mechanism of the sulphonation may probably therefore be expressed by the above scheme ($S = SO_3H$):

Copper and Silver Salts of the Isomeric Sulphonic Acids.

In seeking for a method of differentiating and estimating the isomeric acids, we have studied the behaviour of solutions of their sodium salts towards copper sulphate and silver nitrate. The results are given in the following table:

Acid.	$CuSO_4$.	$AgNO_3$.
2 : 8	Slowly deposits a reddish-orange precipitate.	Rather sparingly soluble precipitate.
2 : 5	Deep red solution, but no precipitate.	No precipitation in moderately concentrated solutions.
2 : 6	Sparingly soluble yellow precipitate.	Very insoluble, white, silky precipitate.
2 : 7	Sparingly soluble orange-yellow precipitate.	Similar, but yellower.

The silver salts of the four isomerides have been prepared in the solid state, and form nearly colourless, crystalline powders. On analysis, the following results were obtained: Found, 2:8, Ag=32·7; 2:5, Ag=32·8; 2:6, Ag=32·9; 2:7, Ag=33·0. Calc., Ag=32·73 per cent.

Determination of their solubilities in water at 15° gave the following results, the numbers indicating parts of water in which one part of the respective acid dissolves: 2:8, 300; 2:5, 70; 2:6, 4900; 2:7, 2800.

We desire to express our thanks to Messrs. Levinstein, Ltd., who have kindly supplied us with the materials required in this investigation.

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MANCHESTER. [*Received, November 12th*, 1917.]

VII.—*The Effect of Temperature and of Pressure on the Limits of Inflammability of Mixtures of Methane and Air.*

By WALTER MASON and RICHARD VERNON WHEELER.

A "LIMIT" mixture of an inflammable gas with air or oxygen can be defined as such that the heat evolved by the combustion of one "layer" of the mixture is sufficient, and only just sufficient, to raise to its ignition-temperature the layer adjacent, so that flame once started in such a mixture continues to be propagated progressively throughout, without the necessity for the continued presence of the source of heat that caused the inflammation.

The self-propagation of flame through the mixture is only possible when the speed of reaction between the combining gases is sufficient to overcome any loss of heat, by radiation, convection, and conduction, under the conditions of its combustion. The speed of reaction is dependent on the temperature that the portion of the mixture which is burning can impart to the portion that is about to burn.

It follows naturally, therefore, that the higher the initial temperature of the mixture the less is the propagation of flame dependent upon the heat generated by combustion, so that the effect of increasing the initial temperature of mixtures of methane and air should be to widen their limits of inflammability, lowering the lower and raising the upper limit.

The effect of pressure on the limits is not so easy to forecast; in point of fact, the results of experiments did not fulfil our anticipations. It will be best to leave discussion of the matter until the experiments have been described.

The Effect of Temperature.

The earliest systematic experiments on the effect of temperature on the limits of inflammability of gaseous mixtures seem to have been by Bunte and Roszkowski in 1890 (*J. Gasbeleuchtung*, 1890, **33**, 491, 524, 535, 553). The mixtures were ignited electrically in a spherical vessel of 35 c.c. capacity. Apart from the fact that it is impossible to judge accurately as to the propagation of flame in such a vessel, something must have been radically wrong with Bunte and Roszkowski's experimental arrangements, for they recorded no marked change in the limits for mixtures of methane

and air when the initial temperature of the mixtures was raised from 15° to 300°.

Taffanel (*Compt. rend.*, 1913, **157**, 593) examined the effect of increased temperature on the lower limit for mixtures of methane and air by passing an electric spark in the mixtures, after introducing them into a tube at the required temperature, and observing whether or no inflammation was propagated throughout the mixture. His results were as follow:

Initial temperature of mixture	20°	175°	237°	312°	555°	690°
Lower limit, methane in air, per cent.	5·80	5·25	4·75	4·30	3·40	3·00

Taffanel did not state the dimensions of his tube, the position of the point of ignition of the mixtures, or the direction of travel of the flames; but from his results, which, as will be seen later, closely correspond with our own, we conclude that a rather wide and short tube was used and that ignition was at the top, the flames being propagated vertically downwards.

Burrell and Robertson (United States Bureau of Mines, Technical Paper No. 121, 1916) repeated Taffanel's experiments, using a Hempel bulb of 100 c.c. capacity as the explosion vessel and igniting the mixtures near the top by an electric spark. The bulb was heated in an electric furnace, and whether or no flame had propagated throughout the mixture was judged by analysing the products of combustion. The results recorded were:

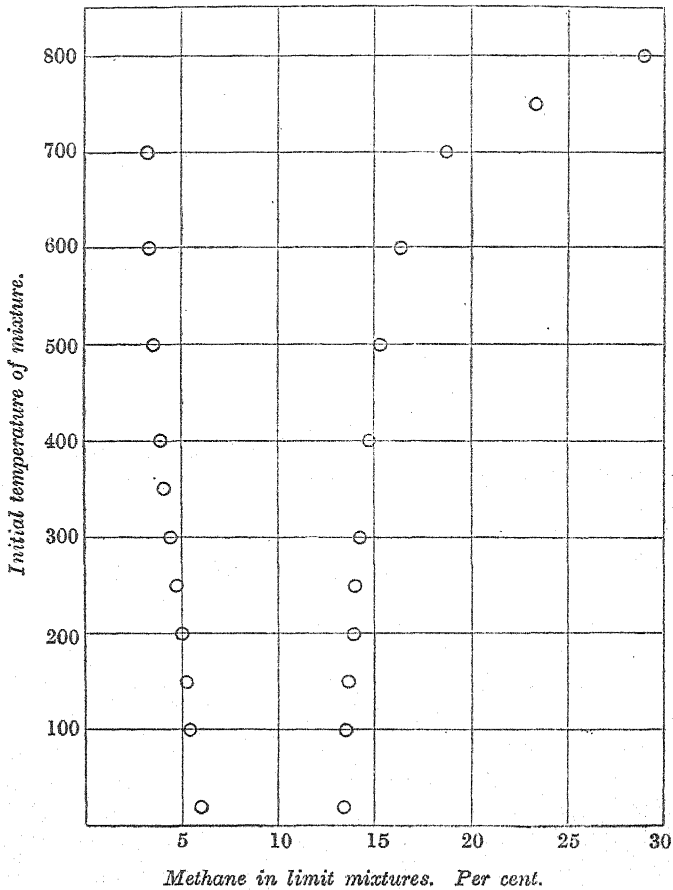
Initial temperature of mixture.	25°	200°	300°	400°	500°
Lower limit, methane in air, per cent.	5·46–5·56	4·98–5·15	4·75–4·88	4·47–4·55	3·75–4·00

Accurate observation of the propagation of flame in a vessel that is totally enclosed in an electric furnace presents some difficulty. It is not easy to judge, for example, of the extent of downward propagation of flame in a tube by an arrangement of mirrors, since the flame is viewed end-on; and analysis of the gases remaining after flame has passed, not altogether satisfactory as a means of judging whether flame has travelled or has just failed to travel throughout the vessel with lower-limit mixtures, gives quite misleading results with the upper-limit mixtures where much of the combustible gas remains unburnt or incompletely burnt.

For our experiments we have made use of the fact that the limits for upward propagation of flame are wider than for downward propagation (T., 1914, **105**, 2591) to aid in observing whether

or no flame travelled throughout the mixtures at different temperatures, in the manner described in the experimental portion of this paper. The criterion of inflammability adopted was self-propagation of flame downwards. The gaseous mixtures were stored over

FIG. 1.



a mixture of equal parts by volume of glycerol and water in glass gas-holders, whence they were introduced into the previously heated and evacuated explosion vessel; they were thus saturated with water vapour at the room temperature (20°). The results are given in the table that follows and diagrammatically in Fig. 1.

Initial temperature.	Downward propagation of flame in mixtures of methane and air. Methane, per cent. Lower limit.	Upper limit.
20°	6·00	13·40
100	5·45	13·50
150	5·20	13·60
200	5·05	13·85
250	4·60	14·00
300	4·40	14·25
350	4·15	not determined.
400	4·00	14·70
500	3·65	15·35
600	3·35	16·40
700	3·25	18·75
750	—	23·60
800	—	29·00

The mixtures were allowed to remain during two seconds in the explosion vessel (which had been previously brought to the required temperature) before the passage of an electric spark to cause ignition. This length of time was sufficient to ensure that the gases attained the temperature of the enclosure (compare Burrell and Robertson, *loc. cit.*, p. 6), and at the same time, except perhaps at the highest temperatures, did not admit of appreciable combustion on the surface of the vessel before the spark was passed.

Consider first the lower limit. Progressive increase of the initial temperature causes a corresponding decrease in the amount of methane required in the air to enable self-propagation of flame to take place. Our determinations agree closely with Taffanel's, and therefore disprove Bunte and Roszkowski's results. With an initial temperature of 750°, a mixture containing 3·00 per cent. of methane ignited without being sparked (and flame was propagated throughout) as soon as it entered the explosion vessel, the rate of reaction on the surface of the explosion vessel at this temperature being sufficiently rapid to cause self-heating of the mixture. At 700° no ignition occurred with a 3·20 per cent. mixture by the walls of the vessel, nor was flame propagated throughout such a mixture when an electric spark was passed; for complete propagation of flame at this temperature the mixture had to contain 3·25 per cent. of methane. Under the conditions of these experiments, therefore, the ignition-temperature (that is, the temperature at which rapid self-heating takes place) of a 3 per cent. methane–air mixture can be regarded as between 700° and 750° (compare Taffanel, *loc. cit.*, p. 597).

Just as the lower limit is lowered by increasing the initial temperature, the upper limit is raised. The extent to which the limit is raised increases regularly with the initial temperature of

the mixture until 600° is exceeded, after which there is a considerable rise in the rate of increase (see Fig. 1). This is probably due to reaction between methane and oxygen on the surface of the explosion vessel being sufficiently rapid with high concentrations of methane at temperatures above 600° to alter the constitution of the mixture during the two seconds that elapse between its introduction into the heated explosion vessel and the passing of the spark. We know that with excess of methane in air, carbon monoxide and hydrogen (both of which have very high upper limits of inflammability) persist in the products of combustion, and it may be that the early production of these gases is the cause of the abnormal raising of the upper limit of inflammability of mixtures of methane and air at temperatures greater than 600°. That combustion without flame takes place to an appreciable extent above 600° under the conditions of the experiments is shown by the fact that at 700° no ignition could be obtained (with a mixture containing 18·70 per cent. of methane) if the mixture were left in the explosion vessel longer than five seconds before sparking, whilst at 750° an interval of only 1·5 seconds sufficed to render a mixture containing 23·50 per cent. of methane uninflammable. In each of these instances we can assume that the mixtures became uninflammable by deprivation of oxygen consequent on its burning the methane. If, therefore, the formation of carbon monoxide and hydrogen by combustion of methane is the cause of the abnormal raising of the upper limit at these high temperatures, the effect is transitory. Hydrogen would be produced also by thermal decomposition of methane, but the reaction is very slow at temperatures below 900°. In any event, it is clear that the results obtained at temperatures above 600° do not properly represent the upper limits for self-propagation of flame in mixtures of *methane* and air.

It may be mentioned that in no instance did ignition of, and propagation of flame in, a high-limit mixture take place through contact with the heated walls of the explosion vessel. At 800°, for example, a spark had to be passed in order to cause flame to travel through the mixture (containing 28·70 per cent. of methane).

The Effect of Pressure.

The effect of initial pressure above atmospheric on the limits of inflammability of mixtures of hydrogen, carbon monoxide, and methane, respectively, with air has been studied by Terres and Plenz (*J. Gasbeleuchtung*, 1914, **57**, 990, 1001, 1016, 1025). The explosion vessel used was an iron cylinder 37 cm. long and 8 cm. in diameter. Ignition was by an electric spark at a point 4 cm.

from the top of the cylinder and on its vertical axis. The criterion of inflammability was, therefore, self-propagation of flame downwards. Whether or no flame had passed throughout the mixture was judged by analysing the products of combustion.

For methane (firedamp from Kissarmas, Transylvania, containing 99·1 per cent. of methane), Terres and Plenz obtained the results shown in the tables that follow.

Lower Limit.

Methane in mixture. Per cent.	Initial pressure. Mm. mercury.	Methane burned. Per cent.
6·00	760	99
6·00	1520	22
6·00	2280	11
6·00	3800	7
6·15	1520	99
6·15	2280	26
6·15	3800	13
6·23	1520	100
6·23	2280	100
6·23	3040	31
6·23	3800	17
6·41	3800	100
6·41	4560	98
6·41	5320	50
6·41	6080	30
6·41	7600	12
6·44	5320	100
6·44	6080	98
6·44	6840	52
6·58	7600	100

Upper Limit.

Methane in mixture. Per cent.	Initial pressure required for propagation of flame. Mm. mercury.
12·98	760
13·35	2280
13·65	4560
13·98	6840

With upper-limit mixtures, according to Terres and Plenz, either the mixture did not burn at all under the conditions of their experiments or flame travelled throughout. No partial propagation of flame took place as with the lower-limit mixtures. Their experiments can be summarised in the statement that an increase of the initial pressure of the mixtures to 10 atmospheres

raised the lower limit (downward propagation of flame) from 6·0 to 6·5 per cent., and also raised the upper limit from 13·0 to 14·0 per cent.

Burrell and Robertson (*loc. cit.*) also studied the effect of pressure on the limits of inflammability of mixtures of methane and air, using the same apparatus as for their work on the effect of temperature. Their experiments were mainly at pressures less than atmospheric, but they recorded that "increasing the initial pressure up to 5 atmospheres had no effect in changing the low limit of complete propagation" (p. 10). At reduced pressures, they found that the limits were narrowed, until at pressures between 250 and 300 mm. of mercury it was impossible, under the conditions of their experiments, to obtain self-propagation of flame in any mixture of methane and air.

Our experiments at reduced pressures have been made with initial temperatures of 20°, 250°, and 500°. The same apparatus was used as for the experiments with different initial temperatures at atmospheric pressure. The results are shown diagrammatically in Fig. 2.

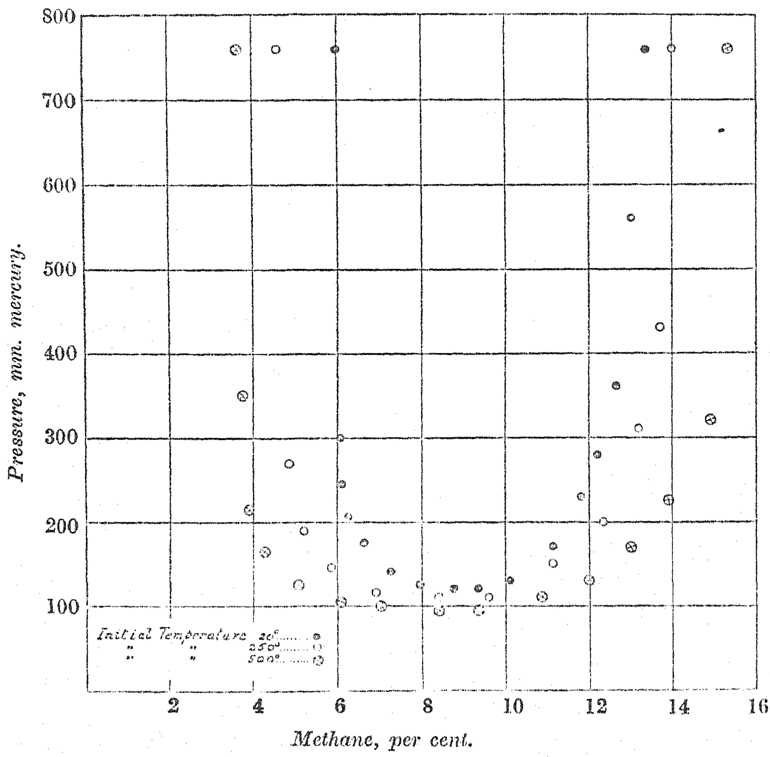
The fact that Burrell and Robertson were unable to obtain self-propagation of flame in any mixture at pressures less than 300 mm. (at atmospheric temperature), whereas we found the limiting pressure to be 120 mm., is explicable on the assumption that their means of ignition was inadequate. For example, a mixture of methane and air containing 9·5 per cent. of methane can be ignited at atmospheric pressure by the secondary discharge from an "8-inch" *X*-ray coil at a spark-gap of 1 mm. between platinum points when the current broken in the primary circuit (the trembler being locked) is about 0·5 ampere; but when the pressure of the mixture is reduced to 100 mm., it is necessary to break a current of more than 7 amperes in the primary circuit of the same coil in order to obtain a secondary discharge at a 1 mm. gap capable of igniting it (T., 1917, **111**, 130). Burrell and Robertson's results express, not the limiting pressure for *self-propagation of flame* in any mixture of methane and air, but the limiting pressure for *ignition* by a secondary discharge of the particular intensity employed by them.

Examination of Fig. 2 shows that at atmospheric temperature the mixtures of methane and air in which flame is propagated (downwards) most readily, as evinced by their having the lowest limiting pressure, contain between 8·75 and 9·40 per cent. of methane.

The same conclusion can be drawn from the experiments by Burgess and Wheeler on "limit" mixtures of methane, oxygen,

and nitrogen (T., 1914, **105**, 2596). Those experiments showed that by the gradual substitution of nitrogen for the oxygen in air the limits were narrowed until, when the "atmosphere" contained only 13·45 per cent. of oxygen, they lay between 6·50 per cent. (lower) and 6·70 per cent. (upper) of methane. From the partial pressures of the gases, the percentages of methane in the atmospheric air contained in these limit mixtures can be calculated, the presence of the excess of nitrogen and of methane (above that

Fig. 2.



required for complete combustion by the oxygen) being regarded as equivalent to a reduction of pressure. This calculation gives 9·2 per cent. of methane in air as the mixture that propagates flame most readily.

The mixtures of methane and air most readily ignited by a secondary discharge, or by the break-flash ("momentary arc") produced at the point of fracture of a metallic electric circuit (continuous current), contain between 8·0 and 8·6 per cent. of

methane, whilst the mixtures in which the "uniform movement" of propagation of flame is most rapid contain between 9·5 and 10·0 per cent. of methane (T., 1914, **105**, 2607).

The range of mixtures over which propagation of flame occurs most readily thus lies mid-way between the range over which ignition (by electrical means) is easiest and the range over which the flames are fastest. It might be argued from this that ease of propagation of flame in a series of mixtures of methane and air is dependent about equally on the ease of ignition of the mixtures and on the ratio $T-t/t-\theta$ (see T., 1917, **111**, 1044). It must be remembered, however, that the ignitibility of the mixtures, as shown by the intensity of the secondary discharge or the primary break-flash required to ignite them, is not necessarily a measure of their ignitibility by heated gases during the propagation of flame.

The effect of raising the initial temperature of the mixtures is to widen the dilution limits at all pressures, and the limiting pressure for the self-propagation of flame in any mixture is lowered, though not to a great extent. A point in these experiments that should be noted is the small effect on the limits produced by reducing the initial pressures by as much as half an atmosphere; the effect does not begin to be marked until the pressure is reduced below 300 mm.

For experiments with initial pressures greater than atmospheric, we have used a tube of stout glass into which the previously prepared mixtures could be forced through a condensing syringe in the manner described in the experimental portion of this paper. The criterion of inflammability was, as before, propagation of flame downwards. The results were as follow:

Initial pressure. Mm. mercury.	Lower limit. Methane, per cent.	Upper limit. Methane, per cent.
760	6·00	13·00
1250	6·05	13·15
2100	not determined.	13·35
2900	6·20	13·60
3350	6·25	not determined.
3750	not determined.	13·80
4650	6·40	14·05

We thus confirm Terres and Plenz's results. For the lower-limit mixtures, our values agree closely with theirs, but we obtained a greater raising of the upper limit by increasing the pressure than they recorded. This, we think, is due to Terres and Plenz not having used a sufficiently powerful source of ignition, for they have stated that the mixtures either did not ignite at all or flame travelled throughout them. This is contrary to our ex-

perience, for we obtained many mixtures at high pressures in which flame travelled only part of the way down the tube. Mixtures of methane and air containing more than 11 per cent. of methane require a secondary discharge of considerable intensity to ignite them, and the intensity required increases rapidly with increased methane content. Thus, a mixture of methane and air, at atmospheric pressure, containing 12 per cent. of methane, can be ignited by the secondary discharge from an "8-inch" *X*-ray coil across a spark-gap of 3 mm. when a current of 7·5 amperes is broken in the primary circuit (the trembler being locked), whereas a mixture containing 13 per cent. of methane requires 15 amperes, and one that contains 14 per cent. 32 amperes. On the other hand, an increase of the pressure (above atmospheric pressure) of any of the mixtures renders it capable of being ignited by a discharge of slightly less intensity (T., 1917, **111**, 411).

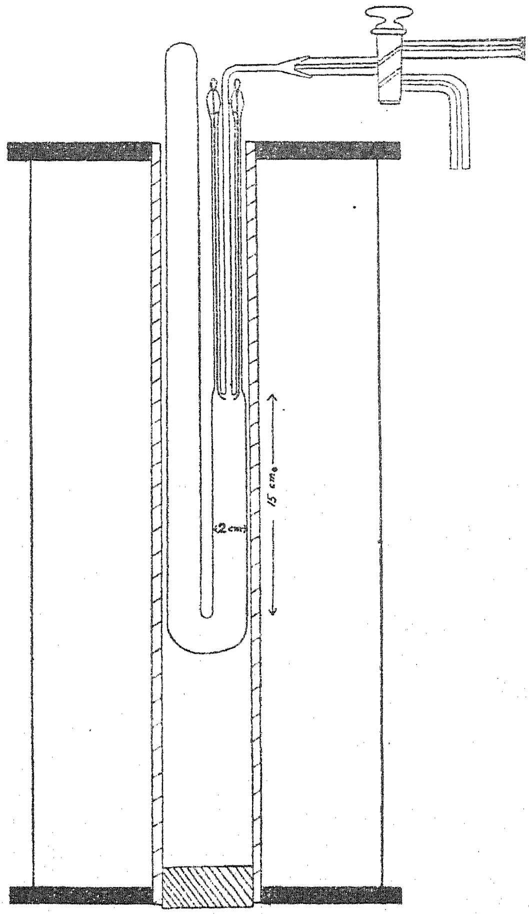
It is easy to see, therefore, by the manner in which they expressed their results, how Terres and Plenz confused the inability of their secondary discharge to ignite some of their mixtures with incapability of the mixtures to propagate flame. They recorded, for example, that a mixture containing 13·65 per cent. of methane did not propagate flame—did not burn at all—when the initial pressure was 6 atmospheres; on raising the pressure to 7 atmospheres (when the mixture would be rendered more readily ignitible), flame was propagated throughout.

Leaving differences in degree aside, however, we are in agreement with Terres and Plenz in observing a raising of both the lower and the upper limit with increased initial pressure (above atmospheric), and we find the results difficult to explain. From the law of mass action, we anticipated that increased pressure, if it had any appreciable effect after atmospheric pressure had been passed, would widen the limits on both sides. If the widening of the upper limit be explained by mass action, what is the reason for the narrowing of the lower limit?

According to the kinetic theory, loss of heat from gases by conduction and radiation is independent of the pressure. When attempting to put this deduction from the kinetic theory to experimental proof, however, Kundt and Warburg (*J. de Physique*, 1876, **5**, 118) found that unless the pressure of the gas was low, the loss of heat due to conduction was masked by that arising from convection currents. It may be, therefore, as Terres and Plenz have suggested, that the loss of heat from a gas at high pressure is due to a greater extent to convection than to conduction, and increases with the pressure. According to this explanation, the upper limit should also be narrowed, and when hydrogen

or carbon monoxide is the combustible gas this is so. What must be regarded as the abnormal behaviour of mixtures of methane and air under pressure at the upper limit requires further study.

FIG. 3.



EXPERIMENTAL.

The apparatus used for determining the limits of inflammability at different temperatures and at pressures less than atmospheric is shown in Fig. 3. It consisted essentially of a U-tube of transparent quartz, the limbs of which were close together, fixed vertically in a tube furnace which could be heated electrically. One limb of the U-tube was 15 cm. long and had a capillary

extension which was fitted, by means of a ground joint, with a glass three-way tap, of the form shown in the diagram, to make connexion with either a vacuum pump or a gasholder and mercury manometer. The other, longer, limb (35 cm.) was sealed at the top, which projected above the level of the furnace. The electrodes for igniting the mixtures were platinum wires led into the quartz tube, immediately below the capillary extension, through capillary side-tubes, the upper ends of which were closed by plugs of glass ground in, through which the platinum wires were sealed. The spark-gap was 4 mm.

Since the limits for upward (or horizontal) propagation of flame are wider than for downward propagation, a mixture which on ignition enabled flame to travel just the full length of the shorter limb of the U-tube easily carried flame up the longer limb, and its appearance could be observed in the portion of the tube above the furnace, either directly or, as was found more convenient during experiments at low pressures, in a mirror inclined at an angle of 45° fixed above the top of the tube and enclosed in a darkened box.

Ignition was caused by a short series of sparks from an "8-inch" *X*-ray coil, with a current of 15 amperes in the primary circuit. The intensity of this discharge with a 4 mm. spark-gap was well in excess of the minimum required for the least easily ignitible mixtures, whilst the length of the tube was sufficient to ensure that the initial impetus imparted to the flames by the source of ignition had died away before the bottom was reached.

For the experiments at high pressures, a tube of thick glass 18 cm. long and of 2 cm. internal diameter was employed, fixed vertically. The tube was provided at the top with a high-pressure three-way tap of capillary bore, to make connexion with either a vacuum pump or a condensing syringe in communication with a gas-holder containing the mixture to be experimented with. A high-pressure tap at the bottom of the tube communicated with a Bourdon pressure gauge. The electrodes were platinum wires sealed into the glass at the top of the tube, the spark-gap being 4 mm. A secondary discharge of the same intensity as for the experiments in the quartz tube was used to ignite the mixtures. The lower third of the tube was covered on the outside with black paper, in which a horizontal slit 2 mm. wide was cut at a distance of 15 cm. from the point of ignition; flame was judged to have travelled throughout the tube if it was observed to pass this slit.

For the experiments at different temperatures, the method of procedure was to obtain two mixtures, differing by 0·10 per cent. of methane, the one enabling flame to appear in the longer limb

of the quartz U-tube, whilst with the other no flame appeared. The mean percentage of methane in the two mixtures was taken as the limiting percentage. For the experiments at different pressures, two pressures were obtained for a given mixture, differing by 10 mm. of mercury at pressures below atmospheric or by 50 mm. at higher pressures, such that at one pressure flame appeared in the prescribed manner, whilst at the other it did not. The mean pressure was taken as the limiting pressure for the particular mixture under the conditions of the experiment.

The methane was obtained from a natural source of firedamp and purified by liquefaction. The mixtures with air (free from carbon dioxide) were prepared in glass gas-holders over glycerol and water, and were analysed before use.

[*Received, November 23rd*, 1917.]

VIII.—*The Relation of Position Isomerism to Optical Activity. Part XI. The Menthyl Alkyl Esters of Terephthalic Acid and its Nitro-derivatives.*

By JULIUS BEREND COHEN and HANNAH SMITH DE PENNINGTON.

IN a former paper (T., 1916, **109**, 222), a series of menthyl alkyl esters of phthalic and 3-nitrophthalic acid were prepared and examined, with the following results: whilst the free carboxyl group in the acid menthyl ester raises the molecular rotation nearly 100° ($[M]_D^{20}$ −332°) above that of menthyl benzoate ($[M]_D^{20}$ −239°), the average rotation of seven menthyl alkyl esters ($[M]_D^{20}$ −243°) did not differ greatly from that of menthyl benzoate—in other words, the proximity of the carboxyl group raises the rotation, whilst that of the ester group produces little effect.

In the case of the parallel series of terephthalic esters, which is the subject of the present paper, the main difference in structure lies in the separation of the two carboxyl groups. One might therefore expect that, like the menthyl alkyl esters of phthalic acid, the alkyl ester group would have little or no influence on the active group, and that the molecular rotations of these substances would be of the same order as that of menthyl benzoate. This anticipation has been realised, the average molecular rotation of seven menthyl alkyl esters of terephthalic acid being $[M]_D^{20}$ −254°. In this case, the average rotation is somewhat higher

than that for the corresponding menthyl alkyl phthalates ($[M]_D^{20}$ $-243°$). In spite of numerous attempts, it was found impossible to obtain the acid menthyl ester in the crystalline state, but the amorphous product prepared by the semi-hydrolysis of dimenthyl terephthalate gave the correct numbers on analysis, and may be regarded as fairly pure. Its rotation was $[M]_D^{18}$ $-259{\cdot}2°$.

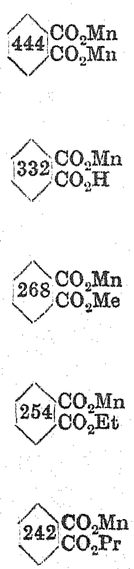
It therefore appears that the carboxyl, like the nitro-group, whilst raising the rotation of the active group in the ortho-position, has little or no effect in the para-position.

	$[M]_D^{20}$.		$[M]_D^{20}$.
o-Nitromenthyl benzoate ...	$-381°$	*p*-Nitromenthyl benzoate ...	$-237°$
Menthyl hydrogen phthalate	-332	Menthyl hydrogen terephthalate	-259

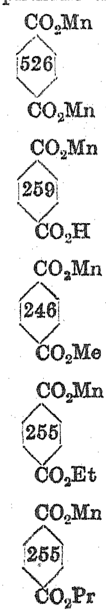
Menthyl benzoate $[M]_D^{20}$ $-239°$.

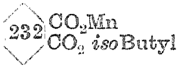
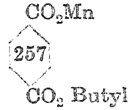
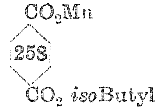
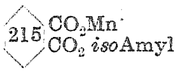
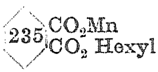
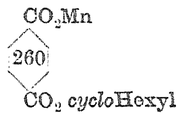
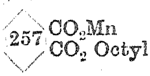
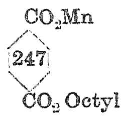
It is somewhat remarkable that whilst the free carboxyl group in the para-position differs little in its effect from that of the ester groups in the same position, both carboxyl and ester group give a higher value than the unsubstituted menthyl benzoate or its *p*-nitro-derivative. The following table gives the parallel series of esters of phthalic and terephthalic acid, molecular rotations, $[M]_D^{20}$ (lævo), being given in round figures within the hexagon (Mn = menthyl).

Phthalic esters.



Terephthalic esters.



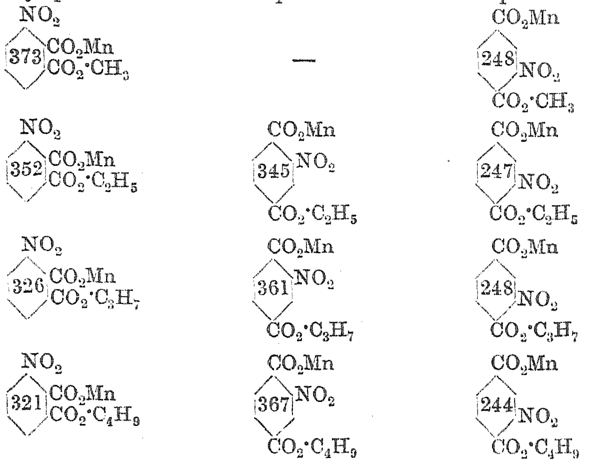
Phthalic esters.	Terephthalic esters.	
		
	—	
		
		

In addition to those points to which attention has been directed, it will be further observed that whilst the rotation of the menthyl alkyl esters of phthalic acid decrease steadily to the *iso*amyl compound and then rise, so that the two end members have the highest rotations, the opposite effect is seen in the case of the terephthalic esters, the two end members possessing the lowest rotations. Further, the molecular rotation of menthyl terephthalate is much higher than that of the corresponding phthalic ester, and about double that of the acid menthyl terephthalate.

If the van't Hoff theory of optical superposition held, and assuming that the two menthyl ester groups in dimenthyl terephthalate to be so far separated as not to influence one another's rotations, the half value ($-263°$) should correspond approximately with that of menthyl benzoate ($-239°$). Unless the hydrogen atom in the para-position lowers the rotation, which does not seem very probable, it would appear that the ester groups in dimenthyl terephthalate influence one another to the extent of raising the rotation about 12°, whilst the average increase for the other members is 15°.

Turning now to the nitro-derivatives, it has been already pointed out that the proximity of the nitro-group to the menthyl ester group greatly increases the rotation, whilst that in the meta- and ortho-position does not. Much the same result has been observed in the two series of menthyl alkyl nitroterephthalates.

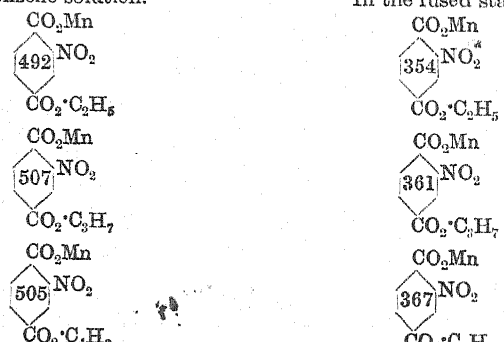
o-Nitro *o*-alkyl menthyl phthalate.	*o*-Nitro *p*-alkyl menthyl terephthalate.	*m*-Nitro *p*-alkyl menthyl terephthalate.



It will be seen from the above table that the proximity of the nitro-group to the active group raises the rotation, being of the same order, although rather lower than that of menthyl *o*-nitrobenzoate ([M] −381°) and the corresponding nitrophthalates ([M] −343° mean). Here again the curious anomaly is observable that whereas in the nitrophthalic esters the rotation falls with the larger alkyl group, the reverse occurs with the corresponding nitroterephthalic esters. On the other hand, the nitro-group in the meta-position with respect to the active group reduces the average value ([M] −247°) to the order of the un-nitrated ester ([M] −254°), that is to say, produces little or no effect.

Another curious anomaly to which attention must be directed is the enhanced rotation of the nitromenthyl esters in benzene solution.

$[M]_D^{20}$. In benzene solution.	$[M]_D^{20}$. In the fused state.



The difference might be ascribed to association, but a determination of the molecular weight of dimenthyl nitroterephthalate (which in benzene has a rotation of $[M]_D^{20}$ $-781°$) by the cryoscopic method in benzene gave a normal result:

0·0851 in 8·79 benzene gave $\Delta^t = -0·1°$. M.W. = 483.

$C_{28}H_{41}O_6N$ requires M.W. = 487.

We are at a loss to account for these abnormal rotations in solution. It suggested, however, a possible explanation of the high values of the *m*-nitro *o*-alkyl menthyl phthalates, all of which being solid at the ordinary temperature were examined in benzene solutions (*loc. cit.*, p. 225); but a comparison of the rotation of *m*-nitro *o*-methyl menthyl phthalate with that of the homogeneous liquid at 100° showed that the solvent had practically no effect. The numbers are:

$[M]_D^{20}$ in benzene.	$[M]_D^{100}$ fused.
$-446°$	$-439°$

The following is a brief summary of the results:

(1) The mutual effect of two menthyl ester groups in the para-position is considerably greater than that of the same groups in the ortho-position.

(2) This is true to a less extent of the alkyl ester group.

(3) The carboxyl group in the para-position has much the same effect as the alkyl ester groups.

(4) The nitro-group in the ortho-position with respect to the active group raises the rotation by about 100°; that in the meta-position has little effect.

(5) The esters with the nitro-group in the ortho-position with respect to the active group exhibit enhanced rotation in benzene solution.

There appears no reason, therefore, to modify the generalisation defined in the former paper (T., 1914, **105**, 1895), namely, that the element or group lying nearest to the active group produces the greatest effect.

EXPERIMENTAL.

The Menthyl Alkyl Esters of Terephthalic Acid.

The method employed in the preparation of these esters may be illustrated in the case of menthyl ethyl terephthalate.

In a small distilling flask fitted with an air condenser was placed a mixture of 12 grams of dry, powdered terephthalic acid and 30 grams of phosphorus pentachloride. The substances were well mixed and warmed gently until the reaction began, being after-

wards heated on the water-bath until solution was obtained. The phosphoryl chloride was removed by distillation on the water-bath under diminished pressure in a current of dry air. The residue was extracted with benzene and filtered to separate excess of phosphorus pentachloride, which is not dissolved. The solvent was removed by heating on the water-bath, and finally under diminished pressure. The yield of acid chloride was 22 grams. To the acid chloride, 20 grams (twice the theoretical amount) of absolute ethyl alcohol was added, and cooled until the first reaction had moderated, when the mixture was heated on the water-bath for half an hour.

The contents of the flask were then dissolved in ether and the ethereal solution shaken up with small quantities of dilute sodium carbonate solution to remove any free acid, after which it was dehydrated over anhydrous sodium sulphate and distilled, first at the ordinary pressure to remove ether, and then under diminished pressure. The yield of diethyl terephthalate was 11 grams (b. p. 148°/2 mm.; m. p. 36—40°).

It was then half hydrolysed as follows: A mixture of 11 grams of the diethyl ester in 14 c.c. of ethyl alcohol and 3 grams of potassium hydroxide in 3 c.c. of water and 14 c.c. of ethyl alcohol was well shaken, when the contents solidified. After heating for half an hour on the water-bath, a little water was added, and the unchanged diethyl ester separated by extracting with small quantities of ether. After removing any residual ether by heating, the solution was cooled and acidified with hydrochloric acid. The solid which separated was collected and crystallised from benzene, in which terephthalic acid is very sparingly soluble.

In this way, 4 grams of pure acid ethyl ester, melting at 168—170°, were obtained. The ester was heated with a large excess of thionyl chloride (8 grams) under reflux on the water-bath until dissolved, any insoluble impurity being removed by filtration. The excess of thionyl chloride was distilled on the water-bath under diminished pressure, and the residue (4 grams), which crystallised on cooling, melted at 27°. The calculated quantity of menthol (3 grams) was added, and the whole heated gradually in an oil-bath to 110—120° for an hour or more, until the evolution of hydrogen chloride ceased. The excess of menthol was then removed by distillation in a current of steam and the residue extracted with ether. The ethereal solution, after shaking with sodium carbonate solution, was dehydrated over calcium chloride and decolorised with charcoal, and then distilled, first on the water-bath and then with the flame and under diminished pressure.

The excess of alcohol used in the preparation of esters of the

higher alcohols was removed by distillation under diminished pressure.

The following table gives the melting and boiling points of the dialkyl esters and the alkyl acid esters.

Dialkyl terephthalate.	M. p.	B. p.	Alkyl hydrogen terephthalate.	M. p.
Dimethyl	140°	—	Methyl, hydrogen	About 230° Indefinite.
Diethyl	36—40	142/2 mm.	Ethyl ,,	168—170
Dipropyl	Liquid	158/4 mm.	Propyl ,,	127—129
Di-*n*-butyl	Liquid	180/4 mm.	Butyl ,,	122—124
Di*iso*butyl	40—43	180/6 mm.	*iso*Butyl ,,	151—154
Di*cyclo*hexyl	75—80	—	*cyclo*Hexyl ,,	160—162
Dioctyl	—	decomposed	Octyl ,,	82— 84

The menthyl alkyl esters obtained by the method described above are viscid liquids with a faint yellow colour which could not be removed by charcoal. The rotations were determined with the pure substances in a 0·302-dcm. tube at 20° and 100°.

Alkyl menthyl terephthalate.	$\alpha_D^{20°}$.	D_4^{20}.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	$\alpha_D^{100°}$.	$D_4^{100°}$.	$[\alpha]_D^{100°}$.	$[M]_D^{100°}$.
Methyl	24·66	1·054	77·49	246·3	23·11	1·000	76·52	243·3
Ethyl I	24·45	1·060	76·38	253·6	21·78	0·998	72·28	240·0
,, II	24·42	1·050	77·45	257·0	21·76	0·991	72·58	240·9
Propyl	23·20	1·041	73·79	255·4	20·72	0·9845	69·69	241·2
n-Butyl	22·39	1·037	71·48	257·3	19·90	0·9848	66·91	240·9
*iso*Butyl	23·30	1·044	73·91	266·1	20·86	0·988	69·92	238·2
*cyclo*Hexyl I	20·90	1·034	67·06	258·9	18·63	1·009	61·14	236·0
,, II	21·42	1·038	68·33	263·7	19·09	1·004	62·92	242·9
Octyl I	17·84	0·999	59·13	246·0	15·96	0·947	55·82	232·2
,, II	17·91	0·999	59·36	246·9	16·03	0·945	56·16	233·6

The following are the analytical results:

Alkyl menthyl ester.	Formula.	Found. Carbon.	Found. Hydrogen.	Calculated. Carbon.	Calculated. Hydrogen.
Methyl menthyl	$C_{19}H_{26}O_4$	71·60	8·20	71·69	8·18
Ethyl menthyl	$C_{20}H_{28}O_4$	72·16	8·48	72·30	8·44
*cyclo*Hexyl menthyl	$C_{24}H_{34}O_4$	74·66	8·78	74·68	8·81
Octyl menthyl	$C_{26}H_{40}O_4$	74·99	9·66	75·01	9·62

Neutral and Acid Menthyl Esters of Terephthalic Acid.

The neutral ester was obtained in the usual way from the acid chloride, the excess of menthol being subsequently removed by steam distillation. It crystallised from hot alcohol in needle-shaped crystals melting at 77—78°.

I. 0·5208 in 25 c.c. benzene in a 2-dcm. tube at 13° gave α −4·91; hence $[\alpha]_D^{13}$ −117·9; $[M]_D^{13}$ −521·1.

At 100° in a 0·302-dcm. tube; D^{100} 0·979.

α_D^{100} – 30·22; $[\alpha]_D^{100}$ – 102·3; $[M]_D^{100}$ – 451·7.

II. 0·5210 in 25 c.c. benzene in a 2-dcm. tube at 12·5° gave α – 4·96; hence $[\alpha]_D^{12·5}$ – 119; $[M]_D^{12·5}$ – 525·9.

At 100° in a 0·302-dcm. tube; D^{100} 0·978.

α_D^{100} – 30·3; $[\alpha]_D^{100}$ – 102·6; $[M]_D^{100}$ – 453·5.

0·1830 gave 0·5100 CO_2 and 0·1569 H_2O. C=76·00; H=9·53.

$C_{28}H_{42}O_4$ requires C=76·02; H=9·50 per cent.

The acid ester was prepared by the semi-hydrolysis of the neutral ester as follows: An alcoholic solution containing 1·3 grams of potassium hydroxide was added to 10 grams of dimenthyl terephthalate, and the mixture heated on the water-bath for two hours. The product was poured into water, and the unchanged neutral ester and menthol extracted with ether. After removing the ether, hydrochloric acid was carefully added to the slightly warm solution, when an oil separated which was dissolved in a small quantity of benzene (in which terephthalic acid dissolves sparingly). The benzene solution was dehydrated with anhydrous sodium sulphate, and the benzene removed first on the water-bath and finally under diminished pressure. The residue consisted of a colourless, resin-like substance which did not crystallise:

0·1805 gave 0·4723 CO_2 and 0·1265 H_2O. C=71·33; H=7·78.

$C_{18}H_{24}O_4$ requires C=71·06; H=7·89 per cent.

0·5160 in 25 c.c. benzene in a 2-dcm. tube gave α_D^{15} –3·52; hence $[\alpha]_D^{15}$ 85·11; $[M]_D^{15}$ 259·2.

Neutral and Acid Menthyl Esters of Nitroterephthalic Acid.

The nitroterephthalic acid was prepared by the method described by Burkhardt (*Ber.*, 1877, **10**, 145). The dimenthyl ester was obtained in the usual way by treating the acid chloride (formed by the action of phosphorus pentachloride on the acid) with the calculated amount of menthol and purifying in the manner already described. After recrystallisation from alcohol, it was obtained in colourless needles melting at 88°:

0·1532 gave 0·3873 CO_2 and 0·1168 H_2O. C=68·93; H=8·47.

$C_{28}H_{41}O_6N$ requires C=68·98; H=8·42 per cent.

0·5084 in 25 c.c. benzene in a 2-dcm. tube gave α_D^{15} –6·53; hence $[\alpha]_D^{15}$ –160·5; $[M]_D^{15}$ –781·2.

At 100° in a 0·302-dcm. tube the pure ester gave α_D^{100} –36·26.

$[\alpha]_D^{100}$ – 116·0; $[M]_D^{100}$ – 564·8.

The acid ester was prepared by the semi-hydrolysis of the neutral

ester with the calculated quantity of potassium hydroxide in methyl alcohol in the manner already described in the previous section. After removing unchanged neutral ester, the acid ester was precipitated by the careful addition of concentrated hydrochloric acid. The solid acid ester was collected and crystallised from aqueous alcohol, when it melted at 75°:

0·1550 gave 0·3515 CO_2 and 0·0924 H_2O. C=61·84; H=6·62.

$C_{18}H_{23}O_6N$ requires C=61·9; H=6·59 per cent.

A second preparation gave the same result.

On reconverting the acid ester into the dimenthyl ester by treating with excess of thionyl chloride and heating the resulting acid chloride with menthol, the product had the same rotation as that found for the ester obtained by the previous method of preparation.

o-Nitro p-Alkyl Terephthalic Esters.

The esters were prepared as follows: The acid menthyl ester was heated with excess of thionyl chloride on the water-bath until a clear solution was obtained, the excess being removed under diminished pressure. The acid chloride was then heated under reflux with an excess of alcohol on the water-bath for about an hour until the reaction was complete. The product was poured into water, the ethereal extract being shaken with small quantities of dilute sodium carbonate solution and dehydrated over calcium chloride, with the addition of animal charcoal. After removing the ether, the nitroalkyl menthyl esters were obtained as viscid liquids, with the exception of the methyl ester, which crystallised in needle-shaped crystals melting at 78—79°.

The rotations were determined in the fused state in a 0·302-dcm. tube at 20° and 100°, and also in benzene solution in a 2-dcm. tube.

	In the fused state.			
o-Nitro *p*-alkyl menthyl terephthalate.	α_D^{20}.	D_D^{20}.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
Methyl	—	—	—	—
Ethyl	−31·56	1·410	−91·58	−345·2
Propyl I	31·09	1·110	92·74	352·6
,, II	31·20	1·126	91·77	358·8
n-Butyl I	29·64	1·098	90·48	366·5
,, II	30·04	1·099	90·51	366·8

	In the fused state.			
o-Nitro *p*-alkyl menthyl terephthalate.	α_D^{100}.	D_4^{100}.	$[\alpha]_D^{100}$.	$[M]_D^{100}$.
Methyl	−30·50	1·093	−92·41	−335·5
Ethyl	28·52	1·08	85·45	322·2
Propyl I	27·79	1·055	87·22	341·0
,, II	27·92	1·063	87·02	340·2
n-Butyl I	26·57	1·043	84·33	341·6
,, II	26·62	1·040	84·74	343·3

o-Nitro *p*-alkyl menthyl terephthalate.	In benzene solution. Gram in 25 c.c. benzene.	α_D^{18}.	$[\alpha]_D^{18}$.	$[M]_D^{18}$.
Methyl I	0·4996	−5·65	−141·4	513·0
,, II	0·3665	4·16	141·7	515·0
Ethyl	0·5100	5·45	130·5	491·8
Propyl	0·6032	6·21	129·7	507·2
Butyl	0·5052	5·04	124·7	505·2

On analysis, the following results were obtained:

Alkyl menthyl ester.	Formula.	Found. Carbon.	Found. Hydrogen.	Calculated. Carbon.	Calculated. Hydrogen.
Methyl	$C_{19}H_{25}O_6N$	62·81	6·85	62·81	6·89
Ethyl	$C_{20}H_{27}O_6N$	63·49	7·26	63·66	7·16
Butyl	$C_{22}H_{31}O_6N$	65·11	7·70	65·18	7·65

m-*Nitro* p-*Alkyl Menthyl Terephthalic Esters.*

The esters were obtained by the semi-hydrolysis of the neutral alkyl esters. The acid alkyl ester thus obtained was converted into the acid chloride, which was then heated with menthol and purified in the usual way.

The following table gives the melting and boiling points of the dialkyl and *m*-nitro *p*-alkyl esters, all of which were crystallised from benzene.

	m-Nitro *p*-alkyl menthyl ester. M. p.	*m*-Nitro *p*-alkyl acid ester. M. p.
Methyl	72—74°	174—176°
Ethyl	48	146—148
Propyl	B. p. 192/6 mm.	135—137
Butyl	B. p. 215/6 mm.	132—134

The rotations were determined in the fused state in a 0·302-dcm. tube at 20° and 100°.

m-Nitro *p*-alkylmenthyl ester.	α_D^{20}.	D_4^{20}.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.	α_D^{100}.	D_4^{100}.	$[\alpha]_D^{100}$.	$[M]_D^{100}$.
Methyl	23·38	1·133	68·31	248·0	20·58	1·096	62·19	—
Ethyl I	22·31	1·127	65·55	247·1	19·55	1·074	60·67	—
,, II	22·29	1·130	65·31	246·2	19·48	1·074	60·06	—
Propyl	21·25	1·130	62·25	248·4	18·80	1·060	58·73	—
Butyl	20·66	1·136	60·23	244·0	18·36	1·057	57·53	—

The following results were obtained on analysis:

Nitro alkyl menthyl ester.	Formula.	Found. Carbon.	Found. Hydrogen.	Calculated. Carbon.	Calculated. Hydrogen.
Ethyl	$C_{20}H_{27}O_6N$	63·60	7·20	63·66	7·16
Butyl	$C_{22}H_{31}O_6N$	65·21	7·60	65·18	7·65

THE UNIVERSITY,
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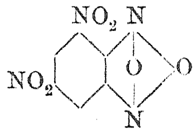
[*Received, December 12th*, 1917.]

IX.—*Nitro-derivatives of* iso*Oxadiazole Oxides and of* iso*Oxadiazoles.*

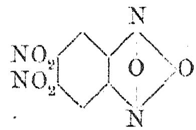
By Arthur G. Green and Frederick Maurice Rowe.

In a previous communication (T., 1913, **103**, 2025) we have directed attention to the so-called "nitro-*o*-dinitrosobenzene and dinitro-*o*-dinitrosobenzene" obtained by Drost (*Annalen*, 1899, **307**, 54) by the nitration of benz*iso*oxadiazole oxide (then termed *o*-dinitrosobenzene).

The dinitro-compound (I) is of special interest, because it



(I.)

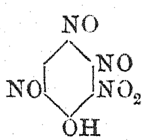


(II.)

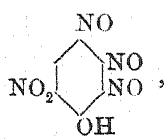
possesses acidic properties, reacting, for example, with potassium hydrogen carbonate to form the potassium salt, $C_6HN_4O_6K,\frac{1}{2}H_2O$ (Drost).

Zincke and Schwarz (*Annalen*, 1899, **307**, 32) consider that the metal in this potassium salt is probably directly attached to carbon and that it is the hydrogen atom between the two nitro-groups which is replaced, for the isomeric dinitro-compound (II) possesses no acidic properties.

As an alternative, Zincke and Schwarz suggest the possibility that the salt may be a derivative of the isomeric compound,



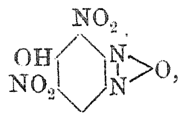
or



,

which is reconverted into the original oxadiazole oxide on treating the salt with acid. The latter hypothesis does not appear to us to afford a satisfactory explanation in view of the improbability that oxygen should wander with such facility from the nitro-group to the carbon nucleus and back again, merely under the influence of weak alkalis or acids. If the acidic properties are to be explained by the presence of a hydroxyl group, it would seem more probable that the latter is formed in the nitration of the benz*iso*-

oxadiazole oxide, the product of which might possibly be a dinitrohydroxybenz*iso*oxadiazole,

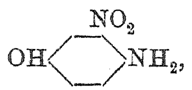


rather than dinitrobenz*iso*oxadiazole oxide.

In order to test this possibility, the pure compound was reduced with titanous chloride. If a hydroxyl group is present, 18 atoms of hydrogen will be required for complete reduction, whereas if there is no hydroxyl group present, 20 atoms of hydrogen will be needed.

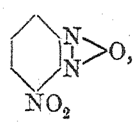
Experiment showed that 20 atoms of hydrogen are required, thus proving the compound to be a true dinitrobenz*iso*oxadiazole oxide. We are therefore reduced to the conclusion that we have here, in fact, an example of hydrogen in the benzene ring possessed of acidic properties.

An attempt was made to obtain a hydroxy-derivative of benz*iso*oxadiazole oxide by the oxidation of nitro-*p*-aminophenol,



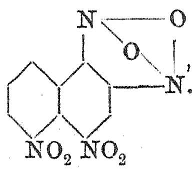
with sodium hypochlorite, with the object of preparing its nitro-derivatives. It was found, however, that oxidation of nitro-*p*-aminophenol under all conditions resulted in the disruption of the ring, accompanied by the formation of chloropicrin, and nothing else could be isolated. The hydroxyl group must therefore be added to the list of substituents already given (T., 1917, **111**, 613) which, when occupying the para-position with respect to the amino-group in a substituted *o*-nitroamine, render the ring unstable to oxidation with hypochlorite.

In view of the interest attaching to dinitrobenz*iso*oxadiazole oxide, it appeared desirable to investigate also the dinitro-derivative of benz*iso*oxadiazole, of which only the mononitro-derivative,



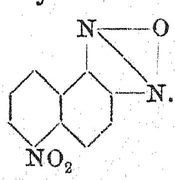
has been prepared by Drost (*Annalen*, 1899, **307**, 69). All our attempts to prepare a dinitro-derivative, however, failed, whether benz*iso*oxadiazole or nitrobenz*iso*oxadiazole was employed, and whether nitration was effected in the cold or at higher temperatures, with one or with more than one molecular proportion of nitric acid.

Finally, we have prepared and examined the previously unknown nitro-derivatives of naphth*iso*oxadiazole oxide and of naphth*iso*-oxadiazole itself. Nitration of naphth*iso*oxadiazole oxide in sulphuric acid solution with three, four, or five molecular proportions of nitric acid, either in the cold or at 50°, gave rise to a single product. On diminishing the quantity of nitric acid to two, one and a-half, or one molecular proportion, the same product was also obtained, although in admixture with unaltered naphth*iso*-oxadiazole oxide. It crystallises in yellow needles melting at 215°, and on analysis with titanous chloride proved to be a dinitro-compound. No trace of a mononitro-compound was obtainable. The dinitronaphth*iso*oxadiazole oxide is very resistant to oxidation, but 3-nitrophthalic acid in sufficient amount for identification was obtained by prolonged boiling with chromic acid and acetic acid. This proves that a nitro-group is situated in each ring, one being in position 5 or 8 and the other in position 4 or 3. Most probably the substance has the constitution



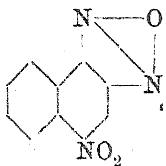
Owing to the destructive decomposition exerted by dilute alkalis, it was not found possible to convert the compound into the corresponding dinitronaphthaquinonedioxime or dinitronaphth*iso*-oxadiazole.

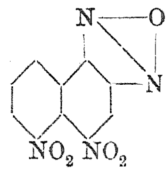
Naphth*iso*oxadiazole differs considerably from naphth*iso*oxadiazole oxide in its behaviour on nitration. When nitrated in sulphuric acid solution with one and a-half molecular proportions of nitric acid, it is completely converted into a product which crystallises in needles melting at 143°. Analysis by titanous chloride showed this product to be a mononitronaphth*iso*oxadiazole. Oxidation with chromic acid and acetic acid produced 3-nitrophthalic acid, showing that the nitro-group is in position 5 or 8. The compound most probably has the constitution



It differs from the nitro-derivatives which follow in that it is not affected by alkalis and does not react with aniline. When the

quantity of nitric acid is increased to 3, 4, or 5, or even 10, molecular proportions, a mixture of two compounds is always obtained, the separation of which may be readily effected by means of alcohol. The amount of the more readily soluble product decreases with increase of the quantity of nitric acid used, and with 10 molecular proportions of nitric acid it is only formed in traces. It crystallises in yellow leaflets melting at 147°. The less readily soluble portion, which constitutes the main product of reaction, crystallises in long, yellow needles melting at 196°. On analysis with titanous chloride, the former product proved to be a mononitronaphth*iso*oxadiazole, the latter a dinitro*iso*oxadiazole. Oxidation of the dinitro-compound produced 3-nitrophthalic acid, whilst from the mononitro-compound phthalic acid was obtained. Hence the nitro-groups are in positions 5 or 8 and 4 or 3 in the dinitro-compound, and in positions 4 or 3 in the mononitro-compound. Their constitution may most probably be represented thus:





The mononitro-compound differs from the previously described isomeride in reacting with alkalis and with aniline. In this respect it is similar to the dinitro-compound. It appears, therefore, that reactivity with alkalis and with aniline is conditioned by the presence of a nitro-group in the same ring as the furazan group. On further nitration, both mononitro-derivatives give rise to the above dinitro-compound.

EXPERIMENTAL.

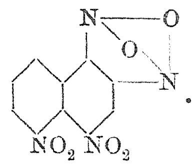
3:5-*Dinitrobenz*isoo*xadiazole Oxide* (*Dinitrobenzfuroxan*) (I).

This was prepared as described by Drost (*Annalen*, 1899, **307**, 54), by the nitration of benz*iso*oxadiazole oxide in sulphuric acid solution. It crystallised from acetic acid in large, yellow needles melting at 172°.

Titration with Titanous Chloride.—0·01 required 29·8 c.c. $TiCl_3$ (1 c.c. = 0·001655 grams Fe).

Calculated as $C_6H_2(NO)_2(NO_2)_2$ = 99·5 per cent., that is, 20H required for reduction.

4(or 3):5(or 8)-*Dinitronaphth*iso*oxadiazole Oxide* (*Dinitronaphthafuroxan*), *probably*



Ten grams of naphth*iso*oxadiazole oxide (T., 1917, **111**, 616) dissolved in 100 c.c. of concentrated sulphuric acid were nitrated by the addition of a mixture of 9 c.c. of nitric acid (95 per cent.) and 30 c.c. of concentrated sulphuric acid. The mixture was cooled at first, and then warmed to 50° and poured on ice. The product, when crystallised from glacial acetic acid or nitric acid, formed bunches of small, prismatic needles melting at 215°.

Titration with Titanous Chloride.—0·0105 required 23·6 c.c. $TiCl_3$ (1 c.c. = 0·001801 gram Fe).

Calculated as $C_{10}H_4(NO)_2(NO_2)_2 = 99{\cdot}7$ per cent., that is, 20H required for reduction.

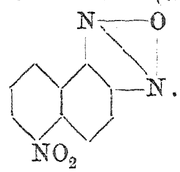
0·131 gave 22·5 N_2 at 16° and 762 mm. N = 20·14.

$C_{12}H_4O_6N_4$ requires N = 20·29 per cent.

Dinitronaphth*iso*oxadiazole oxide, when treated with potassium hydrogen carbonate in the manner described by Drost for the preparation of the potassium salt of dinitrobenz*iso*oxadiazole oxide, does not form a salt. It is, however, sensitive to alkalis, and dissolves with decomposition in boiling sodium carbonate or dilute sodium hydroxide solution, giving a reddish-brown solution with the evolution of ammonia and formation of nitrite. If, however, a little dilute sodium hydroxide is added to an aqueous suspension of the finely divided substance and the mixture cautiously warmed to 30—40°, solution occurs, and after some time a red precipitate separates. This product, which is apparently a salt, crystallises from water in fine, red leaflets. On gently warming the dry product, it decomposes with slight detonation. On acidifying its aqueous solution, a reddish-brown precipitate of impure dinitronaphth*iso*oxadiazole oxide is obtained. When warmed with aniline, dinitronaphth*iso*oxadiazole oxide behaves in an analogous manner to dinitrobenz*iso*oxadiazole oxide. It dissolves with a red colour, and, on the addition of alcohol an anilide separates in reddish-brown needles, which melt and decompose at 166°. This anilide is soluble in alkalis with a red colour, showing that reduction to the dioxime takes place simultaneously with the introduction of aniline into the nucleus.

In endeavouring to ascertain the position of the nitro-groups in dinitronaphth*iso*oxadiazole oxide, various methods of oxidation were tried. The substance is not affected by boiling with dilute or fuming nitric acid, and only by prolonged boiling with chromic and acetic acids was a small quantity of 3-nitrophthalic acid obtained. This crystallised in yellow prisms melting at 218°, and gave the anhydride melting at 163°.

5(or 8)-*Nitronaphth*iso*oxadiazole* (*Nitronaphthafurazan*),



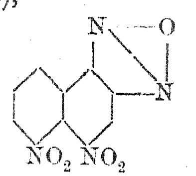
A solution of 10 grams of naphth*iso*oxadiazole in 100 c.c. of concentrated sulphuric acid was nitrated in the cold by adding a mixture of 3·6 c.c. of nitric acid (95 per cent.) and 15 c.c. of concentrated sulphuric acid. The product crystallised from nitric acid in almost colourless, silky needles melting at 143°. It is not affected by boiling with aqueous alkalis or alkaline sodium hypochlorite. It does not react with aniline.

Titration with Titanous Chloride.—0·0112 required 20·4 c.c. $TiCl_3$ (1 c.c. = 0·001708 gram Fe).

Calculated as $C_{10}H_5(N_2O)\cdot NO_2 = 99{\cdot}6$ per cent., that is, 12H required for reduction.

Prolonged boiling with chromic and acetic acids converted this nitronaphth*iso*oxadiazole into 3-nitrophthalic acid, melting at 218°, and forming the anhydride melting at 163°.

4(or 3):5(or 8)-*Dinitronaphth*iso*oxadiazole* (*Dinitronaphthafurazan*),



A solution of 10 grams of naphth*iso*oxadiazole in 100 c.c. of concentrated sulphuric acid was treated with a mixture of 9·5 c.c. of nitric acid (95 per cent.) and 25 c.c. of concentrated sulphuric acid. The mixture was cooled at first and then warmed to 40°. The product crystallised from alcohol in long, yellow needles melting at 196°.

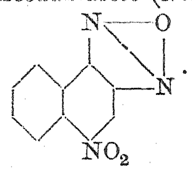
The same substance is obtained by further nitration of either of the two mononitronaphth*iso*oxadiazoles.

Titration with Titanous Chloride.—0·01 required 22·5 c.c. $TiCl_3$ (1 c.c. = 0·001712 gram Fe).

Calculated as $C_{10}H_4(N_2O)(NO_2)_2 = 99·4$ per cent., that is, 18H required for reduction.

*Dinitronaphth*iso*oxadiazole* dissolves in boiling dilute alkalis with decomposition. On the addition of a few drops of sodium hydroxide to a finely divided aqueous suspension and gently warming, a yellowish-brown solution is obtained, from which a brown, flocculent precipitate separates on keeping. This precipitate, when decomposed by acids, does not yield unaltered dinitronaphth*iso*-oxadiazole. Dinitronaphth*iso*oxadiazole dissolves in aniline, on warming, with a reddish-brown colour. On the addition of alcohol, an anilide separates in long, reddish-brown needles melting at 98° and soluble in alkalis. Prolonged boiling with chromic and acetic acids converts the dinitronaphth*iso*oxadiazole into 3-nitrophthalic acid melting at 218°, and forming the anhydride melting at 163°.

4(or 3)-*Nitronaphth*iso*oxadiazole* (*Nitronaphthafurazan*),



On concentrating the mother liquors from which dinitronaphth-*iso*oxadiazole has separated, a second crop of crystals is obtained. After twice recrystallising from alcohol, the product forms yellow leaflets melting at 147°. No method was found by which naphth-*iso*oxadiazole could be completely converted into this compound.

Titration with Titanous Chloride.—0·0102 required 17·7 c.c. $TiCl_3$ (1 c.c. = 0·001801 gram Fe).

Calculated as $C_{10}H_5(N_2O)\cdot NO_2 = 99·9$ per cent., that is, 12H required for reduction.

4-Nitronaphth*iso*oxadiazole dissolves in boiling dilute alkalis with decomposition. On the addition of a few drops of sodium hydroxide to a finely divided aqueous suspension of the compound and gently warming, it dissolves with an orange-red colour, and a brown, flocculent precipitate separates on keeping. This precipitate is decomposed by acids, but does not yield unaltered nitronaphth*iso*oxadiazole. Nitronaphth*iso*oxadiazole dissolves in aniline on warming, with a reddish-brown colour. On the addition of alcohol, an anilide crystallising in red needles melting at 94° and

soluble in alkalis is obtained. Prolonged boiling with chromic and acetic acids converts this nitronaphth*iso*oxadiazole into phthalic acid, from which the anhydride melting at 128° is obtained.

In conclusion, we desire to express our thanks to Miss Eva Hibbert, who has kindly carried out the titrations of these nitro-compounds with titanous chloride.

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X.—*The Mercury Ammonia Compounds. Part. I.*

By MURIEL CATHERINE CANNING HOLMES.

A LARGE number of solid products of the action of aqueous and dry ammonia on mercury salts, either in the presence or absence of the corresponding salts of ammonium, have been described as distinct chemical compounds, but as the solids are in some cases non-crystalline precipitates, and the only evidence of their being chemical compounds is the approximate correspondence of the analyses with simple chemical formulæ, it is not improbable that some of these so-called compounds are solid solutions, the compositions of which vary with the conditions of precipitation, or even mixtures of two distinct phases. Franklin (*Amer. Chem. J.*, 1912, **47**, 361. See also *J. Amer. Chem. Soc.*, 1905, **27**, 835; 1907, **29**, 35; and *Zeitsch. anorg. Chem.*, 1905, **46**, 1), in an excellent summary of the extensive literature on this group of compounds, has emphasised the worthlessness of the evidence on which some of the products obtained have been characterised as chemical individuals. Four modern investigations of Gaudechon (*Ann. Chim. Phys.*, 1911, [viii], **22**, 145), Strömholm (*Zeitsch. anorg. Chem.*, 1908, **57**, 72), Widman (*Zeitsch. anorg. Chem.*, 1910, **68**, 1), and François (*Compt. rend.*, 1900, **130**, 332, 1022), to which reference will have to be made later, have, however, furnished results which were shown to be consistent with the phase rule, and in certain cases with the mass law.

The mercuriammonium compounds can be grouped under the three following classes:

I. The additive compounds of mercury salts and ammonia, of which fusible precipitate, $HgCl_2,2NH_3$, is the best known example.

II. The ammonolysed* compounds, in which one or other of the ammonia residues NH_2, NH, or N take the place of acid radicles in a mercury salt. Infusible precipitate, $ClHgNH_2$, is the simplest representative of this class.

III. The compounds which are both hydrolysed and ammonolysed. For example, the chloride of Millon's base

$$H_2N\cdot Hg\cdot O\cdot HgCl$$

or $HO\cdot Hg\cdot NH\cdot HgCl$.

It should here be mentioned that Rammelsberg (*J. pr. Chem.*, 1888, [ii], **38**, 563), Pesci (*Gazzetta*, 1889, **19**, 509; 1890, **20**, 485), and Gaudechon (*loc. cit.*) advocate the formulation of all three classes of substances as molecular compounds of dimercuriammonium, $ClHg_2N$, with different molecular proportions of water, ammonia, ammonium salts, and mercuric salts. However, Hofmann and Marburg (*Annalen*, 1899, **305**, 191; *Zeitsch. anorg. Chem.*, 1899, **23**, 126), and Franklin (*loc. cit.*) have pointed out that this unusual method of formulation cannot be adopted in the case of the mercury alkyl- and aryl-amines, although these must, in the absence of any evidence to the contrary, be regarded as constituted similarly to the corresponding mercuriammonium compounds. Furthermore, the same authors have shown, in the opinion of the writer convincingly, that Rammelsberg's dimercuriammonium theory is supported neither by analogy nor by any single fact which cannot be as satisfactorily explained by the older and more natural view of the structure of these substances.

The Additive Compounds of Mercuric Chloride and Ammonia.

Mercuric chloride unites with twelve molecular proportions of ammonia when it is treated with liquid ammonia, and at the same time ammonolysis takes place in accordance with the equation (Franklin, *loc. cit.*) $HgCl_2,12NH_3 = ClHgNH_2 + NH_4Cl + 10NH_3$.

The ammonium chloride produced dissolves in the liquid ammonia. It is probable that the change is reversible, and that in the presence of a saturated solution of ammonium chloride in liquid ammonia the ammine would be stable.

By the action of gaseous ammonia on mercuric chloride, fusible precipitate, $HgCl_2,2NH_3$, is formed; but this compound can be obtained as well-defined crystals by dissolving infusible precipitate or the chloride of Millon's base in a hot saturated solution of ammonium chloride and cooling the filtered solution. In this

* The term ammonolyse was introduced by Franklin. Its meaning corresponds with that of hydrolyse.

case, it has been shown by Gaudechon (*loc. cit.*) that the actions are reversible, in accordance with the equations

$$ClHg{\cdot}O{\cdot}HgNH_2 + NH_4Cl \rightleftharpoons 2ClHgNH_2 + H_2O,$$
$$ClHgNH_2 + NH_4Cl \rightleftharpoons HgCl_2,2NH_3.$$

The product obtained by Kane (*Ann. Chim. Phys.*, 1839, [ii], **72**, 215, 337) by heating mercuric chloride in dry ammonia, or by volatilising a mixture of mercuric oxide and ammonium chloride, and supposed by him to be $HgCl_2,NH_3$, is, according to Pesci (*Gazzetta*, 1890, **20**, 485) and Dammer ("Handbuch der Anorg. Chemie," II, 2, 803), probably a mixture.

It is therefore unlikely that any compound of mercuric chloride and ammonia containing a less proportion of ammonia than fusible precipitate has been prepared. In order to test if such a substance is capable of existence, dry ammonia was passed into an ethereal solution of mercuric chloride, the current of gas being stopped before all the mercuric chloride had been precipitated. The flocculent precipitate was washed with ether, left in a vacuum desiccator for several hours, and then analysed.* The analysis furnished the following numbers:

Found: $Hg = 69{\cdot}34$; $Cl = 24{\cdot}30$; $NH_3 = 5{\cdot}98$.
$HgCl_2,NH_3$ requires $Hg = 69{\cdot}52$; $Cl = 24{\cdot}58$; $NH_3 = 5{\cdot}89$ per cent.

This analysis proved that a lower ammine of mercuric chloride must exist, but it did not show that the compound was $HgCl_2,NH_3$, and, as a matter of fact, it will be shown later that the precipitate was almost certainly a mixture.

When the ethereal solution of mercuric chloride was saturated

* As the mercuriammonium compounds lose their ammonia only after prolonged boiling with concentrated alkali, and as the chlorine ion cannot be precipitated completely in the presence of a mercuric salt by silver nitrate, a special method of analysis had to be employed.

To estimate the mercury and ammonium, the salt to be analysed was dissolved in dilute hydrochloric acid: the mercury was precipitated as sulphide with hydrogen sulphide, and the precipitate collected, dried, and weighed in a Gooch crucible. The filtrate and washings were boiled to remove hydrogen sulphide. Sodium hydroxide was then added to the cooled solution, and the ammonia distilled off into a standard solution of acid.

To estimate the chlorine, another weighed portion of the salt was dissolved in dilute sulphuric acid, the mercury in the solution precipitated by hydrogen sulphide, and the sulphine removed by filtration. The hydrogen sulphide in the filtrate was then removed as completely as possible in a vacuum, the small quantity which remained being precipitated with copper sulphate in slight excess. The copper sulphide was filtered off and the chlorine determined in the filtrate by precipitation with silver nitrate.

with ammonia, the composition of the precipitate was approximately that of fusible precipitate, $HgCl_2,2NH_3$.

An attempt was next made to prepare the lowest ammine, namely, that which is stable in the presence of the solid mercuric chloride, by shaking the finely divided fusible precipitate, prepared as above, with a saturated ethereal solution of mercuric chloride. The analysis furnished results in agreement with the formula

$$HgCl_{1\cdot783}\ (NH_2)_{0\cdot217}\ (NH_3)_{0\cdot5581}.$$

The product must therefore have been partly ammonolysed during the washing with ether.

As the analysis appeared to indicate that it would be difficult to obtain a pure substance by the above method of preparation, another mode of preparing the substance, which it was thought might furnish it in a crystalline form, was tried. The experiments with ether had demonstrated that the compound it was desired to prepare was stable in the presence of a saturated solution of mercuric chloride in ether. It ought therefore to be stable in a saturated aqueous solution of mercuric chloride provided that ammonium chloride in sufficient quantity to prevent ammonolysis is dissolved in the water. From such a solution, therefore, an attempt was made to prepare the crystalline ammine.

Infusible precipitate was digested at 100° with solutions of mercuric chloride of different concentrations in an approximately concentrated solution of ammonium chloride, the solution filtered while hot from the undissolved precipitate, and allowed to cool slowly. Well-defined crystals began to separate out when the temperature had fallen almost to that of the laboratory, and gradually increased in amount for several hours. The crystals were rapidly separated from the mother liquor by means of the pump, washed twice with alcohol and twice with ether, left in the vacuum desiccator for several hours, and then analysed. The results, which are recorded in the following table, show that a compound, $3HgCl_2,2NH_3$, undoubtedly exists, and that it is improbable that there is a compound, stable at the ordinary temperature, intermediate in composition between this and fusible precipitate, $HgCl_2,2NH_3$.

In the top row of the table is given the composition of the liquid phase in grams of mercuric chloride in 100 grams of water containing about 42 grams of ammonium chloride, and in the next three rows are the percentages of mercury, ammonia, and chlorine in the solid phase.

Per cent. of	130 grams.	130 grams.	130 grams.	120 grams.
Hg	70·89	70·92	70·78	70·88
NH_3	4·066	4·022	3·98	4·086
Cl..............	—	25·01	25·01	—
Compound separated	$3HgCl_2,2NH_3$	$3HgCl_2,2NH_3$	$3HgCl_2,2NH_3$	$3HgCl_2,2NH_3$

Per cent. of	110 grams.	100 grams.	95 grams.	65 grams.
Hg	70·81	65·46	65·20	64·20
NH_3	3·998	10·70	10·66	11·48
Cl..............	—	—	—	—
Compound separated	$3HgCl_2,2NH_3$	$HgCl_2,2NH_3$	$HgCl_2,2NH_3$	$HgCl_2,2NH_3$

$3HgCl_2,2NH_3$ requires Hg = 70·84; NH_3 = 4·01; Cl = 25·15.
$HgCl_2,2NH_3$ requires Hg = 65·57; NH_3 = 11·13; Cl = 23·13 per cent.

Strömholm claims to have established the existence of a compound of the formula $HgCl_2,H_2NHgCl$, and Gaudechon of the compound $HgCl_2(Hg{:}N{\cdot}HgCl)_2$; but that the work on these compounds needs to be repeated is shown by the following quotation from Franklin's monograph on the mercuriammonium compounds.

"Strömholm was not sure of the existence of a chemical individual of the formula $Hg_5N_2Cl_4$. Gaudechon, on the contrary, obtained results pointing sharply to the formation of this compound, and asserted his belief that no compounds intermediate in composition between $Hg_5N_2Cl_4$ and the normal salt exist; that is, Gaudechon does not accept the existence of a compound of the formula $NH_2HgCl{\cdot}HgCl_2$."

I have therefore repeated Strömholm's work, and have obtained results which confirm his conclusions.

A dilute solution of ammonium chloride was nearly saturated with mercuric chloride. It was then heated at 100° for one or two hours with infusible precipitate, filtered, and left to cool. The precipitate obtained was in the form of a fine, white powder which, after washing and drying, was much more loose and bulky than the other mercuriammonium precipitates. When the ammonium chloride was very dilute, it was necessary to employ as much as 2 litres of solution in order to obtain a quantity of precipitate sufficient for analysis. From the more concentrated solutions of ammonium chloride, the precipitate began to be formed at fairly high temperatures, whereas from dilute solutions it did not separate until the temperature of the laboratory was reached. The precipitate was collected, washed, and analysed by the method described above. The composition of the precipitate varied only slightly with the amount of ammonium chloride in the solution and the temperature at which it was formed.

Gram of NH_4Cl in 100 grams of water.	Temperature of precipitation.	Percentage composition and atomic ratios for solid phase. N.	Hg.	Cl.
1	50—30°	2·83	75·38	—
		[1]	[1·86]	—
1	30—15	2·95	74·66	—
		[1]	[1·79]	
0·3	30—15	—	75·80	—
0·3	30—15	2·76	75·60	—
		[1]	[1·91]	
0·3	30—15	2·83	75·50	—
		[1]	[1·87]	
0·5	30—20	2·78	75·60	20·63
		[1]	[1·90]	[2·91]

$HgCl_2,H_2NHgCl$ requires N=2·675; Hg=76·61; Cl=20·32 per cent.

The approximate constancy of the composition of the precipitate obtained under such varying conditions of temperature and concentration of the liquid phase proves that it is a single phase, whilst the fair agreement of the atomic ratios with those of the compound $HgCl_2,H_2NHgCl$ shows that it can be regarded as this compound with small amounts of the constituents of the solution in solid solution.

Conclusion.

(1) A new additive compound of mercuric chloride and ammonia of the formula $3HgCl_2,2NH_3$ has been prepared.

(2) Strömholm's statement that a compound, $Hg_2Cl_3NH_2$, exists has been confirmed.

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[*Received, November 8th*, 1917.]

XI.—"*Spark-lengths*" *in Hydrocarbon Gases and Vapours.*

By ROBERT WRIGHT.

IN a former paper (T., 1917, **111**, 643), the spark-lengths obtained in various substances were compared with those in air, the temperature, pressure, form of spark-gap, and voltage being the same in each comparison. In the present work, similar measurements have been made for hydrogen, benzene, toluene, and several of the paraffin hydrocarbons, the method employed being identical with that already described.

Each result tabulated is the mean of three or more measurements, which often differed considerably amongst each other, seldom by less than 10 per cent. Still, it is obvious that increase of molecular weight in the series is attended by increase in insulating power, the sole exception noticed being that of *iso*-pentane, which would seem to offer a considerably higher resistance to the passage of the electric discharge than the normal compound, or, indeed, than the following member of the series. The spark-lengths obtained for benzene and toluene are practically identical, and do not differ greatly from that shown by hexane. All measurements were carried out at 138°.

Substance.	Air-gap = 30 mm.	Air-gap = 20 mm.
Hydrogen	80	55
Methane	31	22
Ethane	25	18
Propane	20	15
n-Butane	16	13
n-Pentane	14	11
*iso*Pentane	10	8
Hexane	12	10
Heptane	9	6
Benzene	13	9
Toluene	12	9

The measurements were carried out at the request of Dr. R. V. Wheeler, who supplied all the paraffins employed. The substances used were prepared and purified as follows: *Hydrogen:* prepared from zinc and sulphuric acid, the gas being passed through a series of U-tubes containing glass beads moistened with (*a*) lead nitrate, (*b*) silver sulphate, (*c*) potassium hydroxide. *Methane:* natural marsh gas from a blower in South Wales, purified by liquefaction (CH_4=99·5 per cent.). *Ethane:* from zinc ethyl by the action of water, purified by liquefaction (C_2H_6=99 per cent.). *Propane* and n-*butane:* by the action of nascent hydrogen, from zinc dust and dilute hydrochloric acid, on the corresponding alkyl iodides, purified by liquefaction. The propane contained 98 per cent. of the pure substance and the butane 99·6 per cent. *Pentane* and iso*pentane* were pure liquids obtained from Kahlbaum. *Hexane* and *heptane* were fractionated from petroleum, and each sample consisted of a mixture of isomerides. *Benzene:* this was a pure sample obtained from Kahlbaum. *Toluene:* the sample was fractionated from the commercial product and boiled at 110°.

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[*Received, December 10th,* 1917.]

XII.—*Vacuum Balance Cases.*

By Bertram Blount and William H. Woodcock.

In a recent paper (Blount, T., 1917, **111**, 1035), it was shown that whereas it is generally accepted that a balance by a maker of the highest repute should indicate with certainty a difference of 1 part in 2,000,000, say 0·1 milligram with a load of 200 grams in each pan, yet as a fact six balances of the best kind procurable, tested by three skilled observers at two places, under the most careful conditions and with standard weights, showed variations of 0·4 to 1·6 milligrams over four months.

This fact was ascertained in the course of a research begun about three years ago and, unfortunately, interrupted by the War. At the beginning of the research, the accuracy and constancy of the balance were taken for granted, particularly as so moderate a sensitiveness as 0·1 milligram with a load of 200 grams in each pan was sufficient for the purpose in view.

The main object of the research made it necessary to weigh with the degree of accuracy already mentioned in any gas inert towards the materials composing the balance and the matter to be weighed, or in a vacuum, with approximately the same ease as ordinary chemical and physical weighings are performed in balance cases of the usual construction.

Little work of the kind has been done in this matter, although various vacuum balance cases have been made. Before beginning the work, all recorded instances were investigated, and by the kindness of Mr. Wilfred Airy we were allowed to examine the vacuum balance at the Board of Trade.

Of all the published accounts, the only paper which was of use to us was that of Crookes (*Phil. Trans.*, 1873, **163**, 277). Sir William Crookes explained the whole matter to us personally, and we here record our great sense of obligation to him.

We wished, however, to improve on what had been done, and with the aid of Messrs. Casella, the well-known instrument makers, designed a balance case in which the ordinary wooden balance case was reproduced in every essential, but in gun-metal (Figs. 1 and 2). The top is of plate-glass about 1·9 cm. thick, sufficient to withstand atmospheric pressure when the case is exhausted. The door, which is of plate-glass in a gun-metal frame, is carried on a loose hinge and can be brought up square with the case and tightly closed by means of thumb-screws. All surfaces are scraped as for a surface plate. The glass top carries a pressure of 750

kilos. and the front about 1000 kilos. The mode of raising and lowering the beam is precisely that used for the ordinary analytical balance, but as the balance case must be air-tight, the cam shaft passes through a stuffing box. In like manner, the rider-rod passes through a stuffing box, and as it was found impossible to get this tight with the ordinary movements of a rider-rod, an arrangement by which the rider could be moved by a screw motion was adopted.

The first test showed that the case was not tight. It was naturally supposed that this was due to inaccuracy of mechanical fitting, and various methods of making the surfaces come physically together were tried.

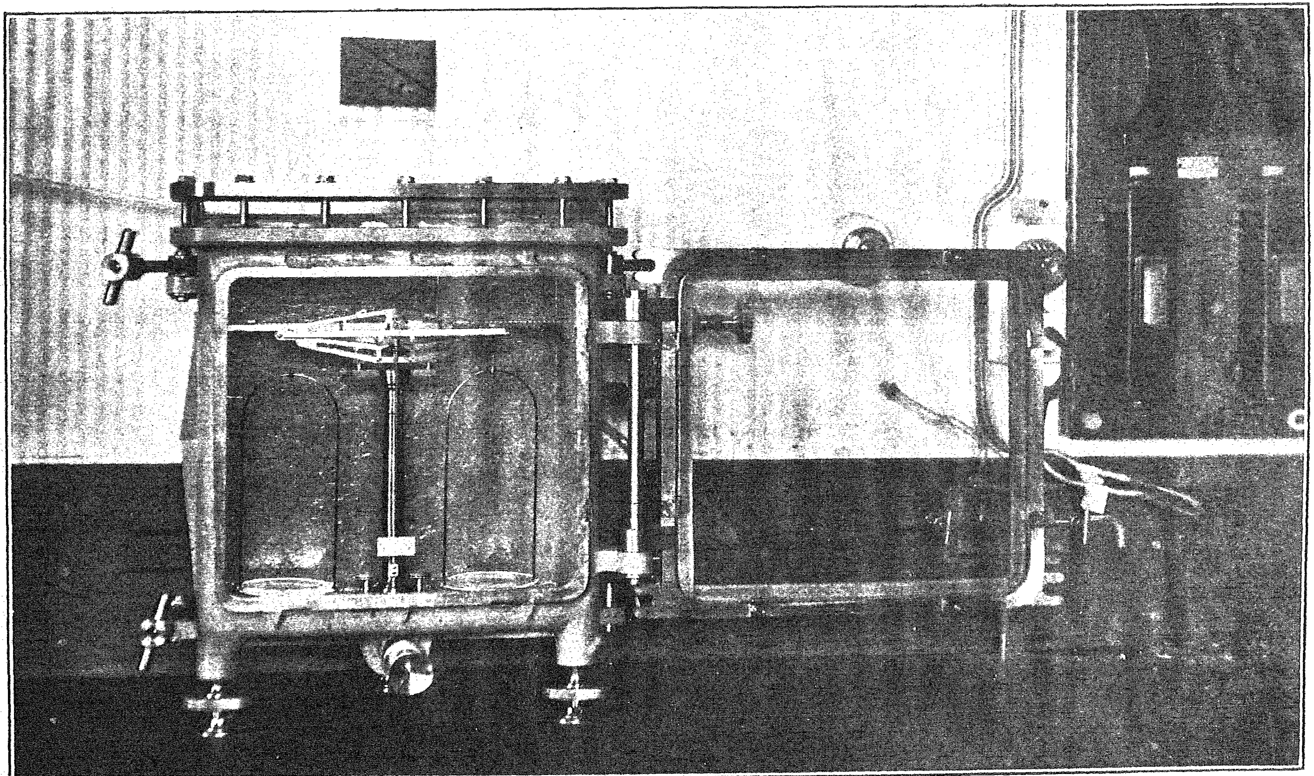
The ordinary mechanical mode of making a tight joint between two metal surfaces is to insert a ring or washer of a softer metal. Lead appeared to be unsuitable, as it might be corroded, so gold was tried as a similar plastic metal. It may be remarked that pure gold is extremely difficult to handle, and many hours were spent in fitting the gold washers accurately to the gun-metal case.

This mode of making the case tight was a failure. Re-machining and scraping of the metal surfaces caused little improvement. Ultimately, it was found that the metal was so porous that to maintain a vacuum within it was impracticable. Accordingly, the gun-metal case was tinned by immersion in a bath of molten tin, and was still porous. It was then enamelled both inside and out, and leakage considerably reduced. We were, of course, aware that gases find their way through metal under high pressure, but were surprised at the large leakage which occurs with such an alloy, mechanically sound and with its pores well blocked with tin, at so small a pressure as 1 kilo. per sq. cm.

As mentioned above, washers were made of very pure and soft gold, and every effort was tried to construct a case satisfactory from an engineering point of view. These efforts failed, and the methods of the chemist had to be adopted. The plate-glass top and door, instead of being fitted to a scraped gun-metal surface, were made tight with vacuum grease applied to the same surfaces. The gun-metal cocks, two sets of which were tried, were abandoned in favour of glass. With these improvements, the case was fairly satisfactory.

Using a Gaede pump, we were able to obtain a fair vacuum with a leakage of somewhat less than 0·01 mm. per hour. It was necessary, for the object in view, to obtain and keep a vacuum of something like 0·001 mm. for an hour without the continued or renewed use of a pump. In short, it was constancy of condition that was sought.

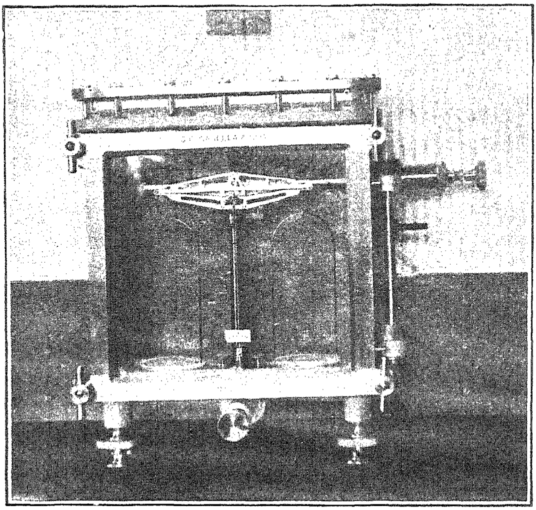
With all its defects, the metal vacuum case has certain merits.



GUN-METAL VACUUM BALANCE CASE, WITH DOOR SHOWN OPEN.

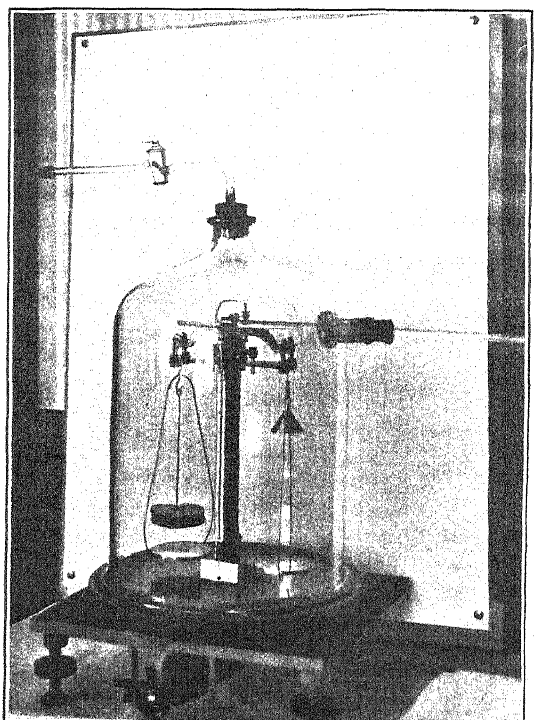
[*To face p.* 82.]

FIG. 2.



GUN-METAL VACUUM BALANCE CASE WITH DOOR CLOSED.
Rider rod on right with screw travel and vertical motion.

FIG. 3.



GLASS VACUUM BALANCE CASE.
Glass rider rod on right ground to fit parallel in glass tube, allowing travel and vertical motion.

It is as near an approach to the ordinary analytical balance, operated in the same way but capable of being used in any given atmosphere (provided it is not corrosive), as has been designed, to the best of our knowledge. It can be used as readily with a moderate plenum as with a vacuum. The shifting of both the main weights and the rider can be easily effected with the single necessity of renewing the atmosphere (or vacuum) when the main weights are moved, in which it is intended to work. With modern methods of producing a vacuum or introducing gases from cylinders containing them under pressure, these operations present no difficulty. It may be noted that all such proceedings take time, and any want of constancy of the balance itself will nullify the results of whatever experiment is in hand.

As it seemed impracticable to make a metal case gas-tight, it was decided to use glass wherever possible. A bell-jar suggested itself as a suitable case for the balance. The size was a difficulty, and the largest procurable had no side tubulus. Accordingly, one was blown on, and we owe thanks to Messrs. Cossor for accomplishing a difficult piece of work (Fig. 3). The bell-jar was ground to fit a thick glass plate carried on a gun-metal plate. Through the middle of the two plates was a tube by which the rising and falling of the beam of the balance could be controlled. A Bunge balance with a 15 cm. beam was used, as we could obtain no bell-jar that would cover a balance with a longer beam. The rider was controlled by a rider-rod capable of the same free movement as that of the ordinary analytical balance; eventually the principle of the ordinary glass hypodermic syringe, used without packing, was adopted, and again we have to thank Messrs. Cossor for accomplishing a difficult piece of work.

The all-glass hypodermic syringe consists of a glass plunger ground to fit the outer tube of the syringe. It is fairly easy to grind conical surfaces to fit, but grinding cylindrical surfaces to a similar accuracy is not so simple and becomes difficult when the material is glass. The difficulty is much enhanced when the length of the cylindrical surfaces is increased. The all-glass hypodermic syringe is a cheap and effective apparatus, but it is only about 5 cm. long and has only a small opening at one end. It was necessary to make a glass rod, ground to fit a glass tube, with such accuracy as to be almost vacuum-tight, having a travel of 25 cm. It would be tedious to record the failures, but at length something which achieved its purpose was prepared.

The outcome of these attempts must be regarded as a success. The balance case can be exhausted to within 0·001 mm., and this vacuum can be kept for more than an hour. The rider can be

moved with the same ease as that of a balance in an ordinary case. The shifting of the larger weights involves breaking the joint between the bell-jar and the plate to which it is ground—a distinct drawback—and a cause of delay. For all that, however, it is an apparatus which may prove useful for the kind of research on which we are intent.

All that is necessary now is a balance which will fit into this case and give constant readings for, say, a year with an accuracy of not less than 1 part in 2,000,000 (0·1 milligram on 200 grams in each pan), and we venture to think that it is not beyond the power of our balance makers to build such an instrument.

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WESTMINSTER, S.W. [*Received, November 30th*, 1917.]

XIII.—*The Constitution of Carbamides. Part V. The Mechanism of the Decomposition of Urea when Heated in Solution with Alkalis and with Acids respectively. The Hydrolysis of Metallic Cyanates.*

By EMIL ALPHONSE WERNER.

WHEN urea, dissolved in a solution of barium hydroxide, was heated, ammonia was evolved as soon as the boiling point was reached, whilst several minutes elapsed before opalescence, due to separation of barium carbonate, appeared. This observation showed that carbon dioxide and ammonia were not simultaneously evolved at the outset of the decomposition, as indicated by the usual equation, adopted to express the change, namely,

$$CON_2H_4 + Ba(OH)_2 = BaCO_3 + 2NH_3.$$

This fact was much more marked when a quantitative examination was made. Thus, when urea and barium hydroxide, in equal molecular proportions, were heated at 100° for two hours in aqueous solution at concentration $N/7$, the amount of ammonia evolved was equivalent to 20·5 per cent. of "hydrolysis," whilst the proportion of barium carbonate precipitated corresponded with only 12·5 per cent. of change, calculated on the basis of the above equation.

It is obvious that the usual interpretation of this reaction is an erroneous one, and it furnishes but another illustration of the manner by which a decomposition of urea has been accepted almost

a priori on the basis of the carbamide configuration without a proper investigation of the change.

The expression 'hydrolysis of urea,' which is generally used with reference to the above decomposition, has been purposely avoided in giving a title to the present paper, since it has been clearly shown that urea was not directly hydrolysed when decomposed in the presence of acids or alkalis.

The relation which exists between urea and ammonium cyanate is a very simple one, namely, whilst the latter is produced from the union of ammonia with cyanic acid in the 'enol' form (HO·CN), urea is the result of the union of ammonia with cyanic acid in its 'keto' form (HN:CO) (T., 1913, **103**, 1013, 2276).

Herein lies the true difference between the two isomerides. When careful attention is given to the fact that dissociation into ammonia and cyanic acid is the first change which accompanies the action of heat on urea, all phenomena connected with its decomposition in solution, either alone or in the presence of acids or alkalis, are easily explained.

An isomeric transformation of urea, as a preliminary to its decomposition, as suggested by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) and by Burrows and Fawsitt (T., 1914, **105**, 609), is a quite unnecessary assumption.

Decomposition of Urea in Aqueous Solution in the Presence of Acids.

This change is represented thus:

$$\text{Phase I.}\quad HN{:}C{<}^{NH_3}_{O} + HCl = NH_4Cl + (HNCO \rightleftharpoons HOCN)$$

$$\text{Phase II.}\quad (HNCO \rightleftharpoons HO{\cdot}CN) + H_2O + HCl = NH_4Cl + CO_2.$$

Since cyanic acid is very rapidly hydrolysed, the velocity of the whole reaction will be regulated by the rate of dissociation of urea (at 100°), when both products of dissociation are removed practically as fast as they are generated.

The basic property of urea is much more pronounced than that commonly associated with acid amides, a fact which in itself may be used as an argument against such a structure,* and when hydrochloric acid is added to an aqueous solution of urea, an equilibrium is established between the base and its hydrochloride. Thus, in a normal solution, Walker and Wood (T., 1903, **83**, 484) found that 45 per cent. of urea hydrochloride was undissociated, a condition

* In this respect urea bears a much greater resemblance to the amino-acids, a type of constitution which is implied by the cyclic formula.

which, according to the author's views, is represented by the following equation:

$$HN{:}C{<}^{NH_2}_{O} + HCl \underset{(b)}{\overset{(a)}{\rightleftharpoons}} HN{:}C{<}^{NH_2,HCl}_{OH}$$

55 per cent. 45 per cent.

Now, since it is only 'free' urea which gives rise to the first phase of the decomposition, the velocity of the change might be expected to diminish with an increase in the concentration of hydrochloric acid. This, however, would be only slightly perceptible at all concentrations much below normal, since by far the greater part of the urea would be in the free state at the outset, and hence only a small amount of change in direction (*b*) would be involved throughout the whole progress of the reaction.

If, on the other hand, most of the urea was 'fixed' at the outset as urea hydrochloride, the velocity of the change would be determined by the diminished rate of dissociation of free urea at low concentration, and this would be maintained fairly constant up to a certain point,* since the change in direction (*b*) would only keep pace with the rate of disappearance of free urea.

The following results, which were obtained by heating solutions of urea with hydrochloric acid to the boiling point under reflux, will suffice to illustrate the points just mentioned.

TABLE I.

(I.) Urea, *N*/5; HCl, *N*/2·5. Molecular ratio, 1:2.

Time.		Urea decomposed.	Time.		Urea decomposed.
1 hour	=	21·25 per cent.	5 hours	=	63·75 per cent.
2 hours	=	33·50 ,,	6 ,,	=	68·90 ,,
3 ,,	=	44·50 ,,	7 ,,	=	78·50 ,,
4 ,,	=	59·25 ,,	8 ,,	=	79·25 ,,

(II.) Urea, *N*/5; HCl, *N*/5. (Equal mols.)

Time.		Urea decomposed.
1 hour	=	22·0 per cent.
2 hours	=	34·5 ,,
3 ,,	=	47·00 ,,
222 minutes	=	50·0 ,,

(III.) Urea, N/2·5; HCl, N/2·5.

Time.		Urea decomposed.
1 hour	=	25·0 per cent.
2 hours	=	44·75 ,,
145 minutes	=	50·0 ,,

A comparison of the results under (I) and (II) (urea = *N*/5) shows the effect of an increase in the concentration of hydrochloric

* The neutralisation of free acid by ammonia would naturally exert a disturbing effect on the above equilibrium, which would be more marked at the higher concentration.

acid in lowering the velocity of the change; the difference was most marked during the third hour, that is, when the concentration of hydrochloric acid, in the case of (II), was very low as neutralisation was approached, since the maximum amount of urea that could be decomposed* in the presence of one molecular proportion of hydrochloric acid is only half of the total present, on account of the simultaneous progress of the two phases of the reaction. The long period required to decompose urea when two molecular proportions of hydrochloric acid were present was due to the slow dissociation of urea as its concentration diminished, and the results show that the velocity of the change was determined solely by the concentration of 'free' urea. The results under (III) furnish additional proof of this; thus it will be noticed that the maximum amount of urea ($N/2\cdot5$) was decomposed in 145 minutes, as compared with 222 minutes, which were required to effect the same amount of change when the concentration of urea at the outset was at $N/5$ (II).

Fawsitt found that it required 2600 minutes to decompose all urea in a solution which contained at the outset urea ($N/8$) and hydrochloric acid ($N/2$), that is, four molecules of acid to one of urea.

Decomposition of Urea in Aqueous Solution in the Presence of Sodium Hydroxide.

Since the acidic property of urea is very feeble, when sodium hydroxide is added to its aqueous solution, an equilibrium represented as follows:

$$HN{:}C{<}^{NH_3}_{O} + NaOH \rightleftharpoons HN{:}C{<}^{NH_2}_{ONa} + H_2O,$$

would only obtain to a small extent when the concentration of both was very high. In solutions below normal, for example, it is certain that nearly if not all the urea would be in the free state. Therefore, according to the dissociation theory, the velocity of decomposition of urea in the presence of sodium hydroxide should be greater than in the presence of hydrochloric acid at all concentrations.

This has been found to be the case, which is contrary to the general result arrived at by Fawsitt (*loc. cit.*). The two phases

* That is, within a comparatively short time, up to the point of neutralisation of the acid. Fawsitt found that in a solution of urea alone ($N/2$), decomposition to the extent of 98·9 per cent. required 450 hours at 99–100°.

of this reaction, which were easily distinguished experimentally, may be represented as follows:

Phase I. $HN:C\langle^{NH_3}_{O} + NaOH = NH_3 + NaOCN + H_2O.$

Phase II. (*a*) $NaOCN + 2H_2O = NH_3 + NaHCO_3.$

In the first phase, cyanic acid is temporarily fixed as alkali cyanate; hydrolysis of the latter quickly follows, and the two phases continue to proceed simultaneously with velocities which vary as the conditions change during the progress of the reaction.

During the earlier stages, sodium cyanate accumulates in considerable quantity in solution, since the velocity of its formation in the first phase is much greater than the speed of its disappearance (by hydrolysis) in the second phase. As the concentration of urea diminishes, the velocity of its dissociation is exceeded by that of the hydrolysis of the alkali cyanate, and hence in the later stages the second phase becomes the predominant change.

The different results obtained after heating urea in solution with sodium hydroxide, under such conditions that ammonia was removed as it was evolved, whilst the concentration was maintained as nearly constant as was possible, are given in the following tables.

The proportion of change under phase I corresponds with the amount of alkali cyanate found in the cold solution at the end of an experiment, whilst phase II represents the amount of alkali cyanate which had been hydrolysed during the progress of the reaction, calculated from the amount of ammonia evolved, after the necessary correction, on the basis of equation (*a*), phase II.

TABLE II.

Urea, *N*/5; sodium hydroxide, *N*/5. Molecular ratio, 1:1.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	17·7 per cent.	4·40 per cent.	22·10 per cent.
2 hours	30·8 ,,	9·0 ,,	39·80 ,,
3 ,, ...	36·0 ,,	18·25 ,,	54·25 ,,

TABLE III.

Urea, *N*/2·5; sodium hydroxide, *N*/2·5. Molecular ratio, 1:1.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	21·25 per cent.	4·15 per cent.	25·40 per cent.
2 hours	32·00 ,,	10·00 ,,	42·00 ,,
3 ,, ...	38·90 ,,	18·80 ,,	57·70 ,,
4·5 ,, ...	36·05 ,,	48·72 ,,	84·77 ,,

TABLE IV.

Urea, $N/5$; sodium hydroxide, $N/2 \cdot 5$. Molecular ratio, 1:2.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	19·05 per cent.	4·52 per cent.	23·57 per cent.
2 hours	27·50 ,,	13·12 ,,	40·62 ,,
3 ,, ...	35·35 ,,	19·82 ,,	55·17 ,,
4 ,, ...	36·10 ,,	28·95 ,,	65·05 ,,

TABLE V.

Urea, $N/5$; sodium hydroxide, N. Molecular ratio, 1:5.

Time.	Phase I.	Phase II.	Urea decomposed.
1 hour	20·0 per cent.	6·75 per cent.	26·75 per cent.
2 hours	28·9 ,,	16·55 ,,	45·45 ,,
3 ,, ...	34·2 ,,	27·65 ,,	61·85 ,,

When the above results are compared with those recorded under table I, it will be seen that the proportion of urea decomposed was greater in the presence of sodium hydroxide than in the presence of hydrochloric acid at similar concentrations.

Whilst the foregoing results are in perfect agreement with the dissociation theory of the mechanism of the change, they appear as a contraversion of the conclusions arrived at by Fawsitt (*loc. cit.*), who found that unless the concentrations of alkali was very high (and that of urea relatively so), the velocity of the change was greater in the presence of hydrochloric acid than in the presence of sodium hydroxide.

All Fawsitt's experiments were made in sealed tubes, and herein lies the cause of the discrepancy, which supplies further evidence in support of the present theory. It is obvious that accumulation of ammonia in solution under pressure would seriously check the dissociation of urea, and so retard the change to an extent which would have no parallel in the case of the decomposition in the presence of an acid, where both dissociation products were removed as fast as they were generated. Thus, when urea and sodium hydroxide, in equal molecular proportions and at concentration $N/5$, were heated for three hours at 100° in a sealed tube, only 33 per cent. of urea was decomposed, as against 54·25 per cent. (exp. 3, table II) when the experiment was performed in an open vessel, all other conditions being equal. It should be noticed that the amount of urea decomposed in the former case is also considerably less than that decomposed in the presence of hydrochloric acid ($N/5$) in an open vessel [table I, (II)].

When the relative effects of acids and alkalis on the velocity of the decomposition of urea are considered, there can be no doubt that in Fawsitt's experiments, on account of the use of sealed tubes, a departure from comparable conditions was quickly brought about.

As a matter of fact, Fawsitt showed that the decomposition of urea was retarded by the presence of ammonium hydroxide or ammonium chloride, whilst such salts as sodium chloride and potassium chloride, although they had but little effect in very dilute solutions, produced a marked increase in the speed of decomposition at normal concentration. Other 'catalysts,' including platinum-black, were found to be without effect, and in the obscure light of the isomeric transformation theory, no explanation could be offered.

The effects in question are obviously in complete agreement with the dissociation theory, which they help to confirm.

Decomposition of Urea in Aqueous Solution in the Presence of Barium Hydroxide.

This reaction was originally proposed by Bunsen as a method for the estimation of urea, based on the amount of barium carbonate formed. As is well known, severe conditions are required to complete the change, namely, very prolonged heating, a high temperature (180—200°), and an excess of barium hydroxide.

It is curious, in view of the above, that the progress of this decomposition has apparently not been investigated.

The two phases of the reaction are represented thus:

$$\text{Phase I.}\quad 2HN{:}C\!\left<\begin{matrix}NH_3\\ |\\ O\end{matrix}\right. + Ba(OH)_2 = Ba(OCN)_2 + 2NH_3 + 2H_2O.$$

$$\text{Phase II.}\left\{\begin{array}{ll}(b) & Ba(OCN)_2 + 3H_2O = BaCO_3 + 2NH_3 + CO_2, \text{ and}\\ (c) & Ba(OCN)_2 + 2H_2O = BaCO_3 + CON_2H_4.^{*}\end{array}\right.$$

The following results were obtained when urea and barium hydroxide in equal molecular proportions were heated at 100° in aqueous solution, and whilst ammonia was removed as it was evolved.

* See page 94

TABLE VI.

Urea, *N*/8; barium hydroxide, *N*/8.

Time.	Phase I.	Phase II.	Urea decomposed.	Calculated on the usual equation. BaCO$_3$ precipitated.	Calculated on the usual equation. NH$_3$ evolved.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1 hour ...	16·0	3·0	19·0	6·0	11·0
2 hours ...	23·9	8·55	32·45	12·5	20·5
3 „ ...	28·7	15·15	43·85	18·5	29·5
4 „ ...	29·9	17·55	47·45	22·5	32·5

The numbers in the two last columns are given to prove the fallacy underlying the usual interpretation of the change. Thus, after one hour, whilst the amount of barium carbonate formed indicated the decomposition of only 6 per cent. of the urea originally present, the ammonia evolved was equal to the decomposition of 11 per cent.; in reality, the amount of urea which had been decomposed was equal to 19 per cent., that is, 8 per cent. of the nitrogen of urea was present in solution as barium cyanate.

In these experiments, phase II commenced (judged from the sudden appearance of opalescence) about seven minutes after phase I had been in progress. Since one molecular proportion of barium hydroxide can theoretically complete the decomposition of two molecular proportions of urea, the results of the two phases should be compared with those under table IV. When the true mechanism of the change is brought to light, it can be readily understood why such severe conditions have been found necessary in order to estimate urea by means of this reaction.

The Stability of Urea in Aqueous Solution and in the Presence of Acid, and of Alkali in the Cold.

After a solution of urea has been heated for a few minutes at 90—100° and subsequently cooled, the presence of the cyanate radicle can be readily proved on addition of silver nitrate. This well-known fact is not explained by the usual ionic theory. Fawsitt found that 450 hours were required to decompose and hydrolyse 98·9 per cent. of the urea originally present in a semi-normal solution at 99°.

If the dissociation products could persist at a constant temperature an equilibrium, represented thus,

$$NH_3$$

$$\swarrow \quad + \quad \searrow$$

$$HN{:}C{<}\genfrac{}{}{0pt}{}{NH_3}{O} \rightleftharpoons HN{:}CO \rightleftharpoons HO{\cdot}CN \rightleftharpoons NH_4{\cdot}OCN,$$

would obtain, and the decomposition of urea and of ammonium cyanate would be completely arrested. The velocity of the change is determined by the very slow hydrolysis of cyanic acid under highly unfavourable conditions, whilst dissociation of urea is checked in consequence.

The progress of the change may be mentally compared to the working of a syphon in which the flow of liquid through the downward tube is seriously checked by a very narrow outlet.

Since urea is not dissociated in solution at the ordinary temperature, an equilibrium between it and ammonium cyanate can only arise on the application of heat. Judging from certain statements in the literature of the subject, the views on this point do not appear quite clear, since it is sometimes stated that the equilibrium is independent of the temperature.

In order to settle the question, a solution of pure urea ($N/2$) in distilled water sterilised by saturation with toluene was tested from time to time with silver nitrate and with barium hydroxide respectively. After nine months, the solution was still neutral, and a negative result was obtained with each reagent.

A similar solution of urea in non-sterilised water gave a marked opalescence with the respective reagents after fourteen days. At the end of six months, the solution contained ammonium carbonate, but no ammonium cyanate, since, after precipitation with barium hydroxide, the carefully neutralised filtrate gave no precipitate on the addition of silver nitrate. This latter result is of interest, since the decomposition of urea in this case was unquestionably brought about, through the agency of urease, by micro-organisms * which had developed in the solution.

A solution of urea ($N/2$) in pure sodium hydroxide ($N/2$) solution, after remaining at the laboratory temperature for five months, showed no change; at the end of twelve months a trace of the cyanate radicle was detected.

A solution of urea in the presence of hydrochloric acid under similar conditions remained unchanged.

Urea therefore does not undergo an isomeric change until the temperature of its dissociation is reached.

Note on the Decomposition of Urea by Urease.

The ease with which urea is decomposed by urease, even at 15—20°, is in striking contrast to its stability in the presence of acids or of alkalis at the same temperature, or when heated alone

* The mycelium of a specific mould was observable in the solution.

in solution. When the remarkable* 'selective' action of the enzyme is remembered (Armstrong and Horton, *Proc. Roy. Soc.*, 1912, **85**, 109), this fact must be considered as additional evidence in favour of a molecular structure of urea peculiar to itself, as shown by the cyclic formula.

It seems probable that the zymolysis of urea is a true case of direct hydrolysis, independent of dissociation as a preliminary to the change. Urease was not found to have an accelerating effect on the hydrolysis of potassium cyanate, nor has it been found possible, so far, to detect the cyanate radicle during the decomposition of urea by the enzyme. The suggestion put forward by Armstrong and Horton (*loc. cit.*) that urease, the solution of which they noted was acid to phenolphthalein, probably acts by combining with urea in virtue of the basic character of the latter, is open to doubt. Urease is markedly amphoteric, a fact which, so far as the author is aware, has not been generally recognised. The alkalinity of a solution of the enzyme towards methyl-orange was found to be greater than its acidity towards phenolphthalein.

The Decomposition of Urea in the Presence of Alcohol.

Burrows and Fawsitt (*loc. cit.*) found that the addition of alcohol to a solution of urea $(N/10)$ + hydrochloric acid $(N/10)$ produced a marked decrease in the velocity of decomposition. This result, they state, "was not exactly what we anticipated," since "alcohol increases the velocity of transformation of ammonium cyanate into urea, and the decomposition of urea is closely related to its formation." The latter remark, of course, is only true so far as the change (dissociation) which gives rise to the first phase of its decomposition is concerned.

The addition of alcohol should undoubtedly produce an increase in the velocity of the decomposition of urea if this is solely dependent on its dissociation and all other conditions are the same. A consideration of the conditions implied by the equilibrium scheme just given will show why this result is not effected. Since alcohol promotes the dissociation of ammonium cyanate, it must also inhibit to a corresponding degree any tendency to its formation at all temperatures above its dissociation point, and hence its presence brings about a limitation on one side which counterbalances its promotive effect on the other. The ulterior effect of

* The behaviour of urease towards seventeen different amino- and imino-compounds, presumably more or less related to urea in constitution, has been examined. In no case was there evidence of decomposition.

alcohol will therefore depend on its power of facilitating or retarding the removal of one or other of the dissociation products, and since a check on the rate of hydrolysis of cyanic acid will be the effect, as suggested by Burrows and Fawsitt from a somewhat different point of view, the velocity of the decomposition of urea will be retarded in consequence. The increased pressure produced by alcohol, particularly at high concentration, and at the higher temperature (98·2°), would also check dissociation of urea.

In the conversion of ammonium cyanate into urea, the promotive effect of alcohol is in no way interfered with, since both dissociation products are removed with great rapidity by the formation of urea at a temperature much below its dissociation point, and hence there is little or no opportunity for hydrolysis of cyanic acid.

It is interesting to note the very much greater velocity of decomposition of urea at 98·2° as compared with that at 71·25° and at 61·05° found by Burrows and Fawsitt. The respective values are represented by the ratios 83·6, 2·77, and 0·715. The fact that urea only commences to dissociate in solution at a fair degree of rapidity above 90° explains the cause of this wide difference.

Mechanism of the Formation of Urea during the Hydrolysis of Metallic Cyanates.

O. and J. Masson (*Zeitsch. physikal. Chem.*, 1910, **70**, 290) have shown that the hydrolysis of potassium cyanate at 80° was completed, in accordance with the equation:

$$(d)\quad 4KOCN + 6H_2O = 2K_2CO_3 + (NH_4)_2CO_3 + CON_2H_4,$$

whilst in the case of barium cyanate the whole of the nitrogen appeared in the form of urea, as represented by equation (*c*) (p. 90).

Ionisation of the cyanate being assumed as the first step, O. and J. Masson have accounted for the formation of urea thus:

$$(A)\quad CNO' + 2H_2O \longrightarrow NH_4^{\cdot} + CO_3''.$$
$$(B)\quad CNO' + NH_4^{\cdot} = CON_2H_4.$$

A somewhat similar suggestion has been offered by Normand and Cumming (T., 1912, **101**, 1859) to explain the formation of urea when pure cyanic acid was hydrolysed in dilute solution, thus:

$$(C)\quad 2H^{\cdot} + 2CNO' + 2H_2O = CON_2H_4 + CO_2.$$

It was suggested, because the alkali cyanates show a neutral reaction, that cyanic acid must be a strong acid, and would, there-

fore, be highly ionised in dilute solution. From this suggestion the author ventures to differ. Alkali nitrites, for example, have a neutral reaction, yet nitrous acid is an extremely weak acid, $K = 6 \times 10^{-4}$, according to Rây and his co-workers (T., 1917, **111**, 414). The properties of cyanic acid are distinctly those of a feeble acid, and the ease with which its ammonium salt is dissociated, whereby urea is formed, is a fact which bears directly on the immediate question.

It must be admitted that an ionic theory, such as is represented by equation (*B*), originally proposed by Walker, or by (*C*), fails to throw any light on the mechanism of the change, since no attempt has been made to show in what way urea is formed from the interaction of the respective ions $NH_4^{\cdot}$ and CNO'. With the deceptive 'carbamide' structure in view, it has evidently been considered useless to attempt to pursue the mysterious changes by which the ions effect such a result. Now an ionic theory is not in agreement with the facts; Walker found, contrary to expectation, that the velocity of the transformation of ammonium cyanate into urea was greater in the presence of alcohol than in the presence of water, and since there must be fewer ions present in the former condition, it has been assumed that the velocity of the interaction (*B*) must be greater in the presence of alcohol. It must be conceded that this is but a speculation, to meet a fact, rather than an explanation. Since alcohol will promote dissociation of ammonium cyanate, whilst diminishing ionisation, the increased velocity of the transformation under such conditions appears as a normal phenomenon in perfect agreement with the author's theory of the change (*loc. cit.*).

The formation of urea from metallic cyanates is explained in a simple manner, on the basis of hydrolytic dissociation * as the first step in the change, thus:

$$KOCN + H_2O \rightleftharpoons KOH + (HOCN \rightleftharpoons HN{:}CO)$$

$$\searrow$$

$$HOCN + H_2O = NH_3 + CO_2 = KHCO_3$$

$$HN{:}CO + NH_3 = HN{:}C{<}\begin{matrix}NH_3\\ |\\ O\end{matrix}, \text{ and } HOCN + NH_3 = NH_4{\cdot}OCN.$$

The following results illustrate how slowly potassium cyanate was hydrolysed in solution at the ordinary temperature.

* Pure potassium cyanate shows a slight alkalinity towards phenolphthalein after immediate dissolution in water.

TABLE VII.

Potassium Cyanate, N/2. Mean $t^{\circ} = 16^{\circ}$.

Time.	KOCN hydrolysed.	Time.	KOCN hydrolysed.
7 days	11·4 per cent.	42 days	81·8 per cent.
13 "	22·4 "	49 "	87·8 "
21 "	43·2 "	56 "	91·6 "
28 "	56·8 "	63 "	94·5 "
35 "	69·7 "	70 "	98·7 "

The amount of urea found in solution at the end of ten weeks was 0·94 gram; from 8·1 grams of potassium cyanate, equation (*d*) would require 1·5 grams of urea. The conditions were less favourable for the formation of urea than when hydrolysis was effected at 80°, at which temperature ammonium cyanate would not be formed.

When potassium cyanate was hydrolysed at 100° under reflux, urea was formed to the extent of 18·44 per cent. of the theoretical, equation (*d*). No urea was found when potassium cyanate (*N*/5) was hydrolysed at 100° in presence of sodium hydroxide (*N*/2·5) (Expts. I, II, and III). It may therefore be safely concluded that no urea would be regenerated during the progress of its decomposition in the presence of sodium hydroxide in an open vessel; on the other hand, a condition favourable to its regeneration, to some extent, would be brought about in a sealed tube, more particularly in the later stages of the reaction. This fact must also be taken into account in considering the results obtained by Fawsitt (*loc. cit.*) for the velocity of the decomposition of urea in the presence of alkalis.

EXPERIMENTAL.

As regards the results given under table I, it is only necessary to point out that the titrations of residual acidity after each experiment were made with methyl-orange as indicator. The urea used (0·6 gram in each case) was twice recrystallised from alcohol. All the experiments were made with the same flask and reflux condenser, and a quiet, continuous ebullition was maintained throughout. Each experiment was duplicated.

The following method was adopted in obtaining the results of the decomposition of urea in the presence of sodium hydroxide.

Expts. tables II–V.—0·6 Gram of urea, 10 c.c. of *N*-sodium hydroxide, and 40 c.c. of water (concentration *N*/5) were heated to the boiling point in a distillation flask (150 c.c.) of resistance glass, carrying a stoppered delivery tube, through which a continuous supply of recently boiled distilled water was maintained, so that the volume of liquid was kept, as nearly as possible, constant

throughout the process of distillation. The ammonia evolved was absorbed in an excess of normal acid contained in a suitable receiver attached to a vertical condenser connected with the distillation flask. At the end of an experiment the residual solution was rapidly cooled under the tap; the cyanate radicle was estimated (1) by precipitation with silver nitrate in the neutral solution, after the 'carbonate' had been removed by barium nitrate and barium hydroxide; the excess of silver nitrate was titrated by Volhard's method; (2) by addition of the solution to an excess of hydrochloric acid, which was afterwards titrated, using methyl-orange as indicator. A lower result was almost invariably obtained by this method; this was due to slight loss of cyanic acid, the odour of which was very noticeable when the liquid was added to excess of normal acid; the solution was allowed to remain, until the odour had disappeared, to ensure complete hydrolysis of cyanic acid before titration. The following examples will suffice to show how the values for the two phases were calculated:

$$0·6 \text{ gram } CON_2H_4 \longrightarrow 2NH_3 = 20 \text{ c.c. } N\text{-HCl},$$
$$NaOCN = 100 \text{ c.c. } N/10\text{-}AgNO_3.$$

Table III. One Hour.—Ammonia evolved = 2·95 c.c. N-HCl.

Sodium cyanate present in residual solution = 21·25 c.c. $N/10$-$AgNO_3$. Hence, phase I = 21·25 per cent.; if hydrolysed, this would be obviously equivalent to ammonia = 2·125 c.c. N-HCl. Hence, omitting the third decimal number, $(2·95 + 2·12) \times 5 = 25·35$ per cent. of urea decomposed, and $25·35 - 21·25 = 4·10$ per cent. phase II.

Table IV. *Four Hours.*—Ammonia evolved = 9·4 c.c. N-HCl.

Sodium cyanate present = 36·1 c.c. $N/10$-$AgNO_3$ = 36·1 per cent. phase I; hence, $(9·4 + 3·61) \times 5 = 65·05$ per cent. of urea decomposed; therefore, phase II, $65·05 - 36·1 = 28·95$ per cent.

A second experiment, in which the residual sodium cyanate was hydrolysed [method (2)], gave ammonia = 3·55 c.c. N-HCl = 35·5 per cent. phase I; ammonia evolved = 9·45 c.c. N-HCl. Hence, 65·0 per cent. of urea decomposed, and phase II = 29·5 per cent.

Whilst no great accuracy is claimed for the values representing each phase, on account of the difficulty experienced in maintaining the volume of solution constant, the order of the results, so far as the amount of urea decomposed was concerned, can be certainly trusted within 2 or 3 per cent., and since this was one of the chief facts which it was sought to prove, no further useful information was likely to be obtained by extending the time of heating beyond three or four hours.

The following is an example of an experiment with barium hydroxide.

Table VI. Four Hours.—Ammonia evolved = 6·5 c.c. *N*-HCl. Barium carbonate precipitated, neutralised 4·5 c.c. *N*-HCl. Hence (from 0·6 gram of urea) amount of urea decomposed = 32·5 per cent. from ammonia estimation and = 22·5 per cent. from amount of barium carbonate precipitated, calculated on basis of usual equation.

Barium cyanate in residual solution = 29·9 c.c. $N/10$-$AgNO_3$. Hence phase I = 29·9 per cent., and $(6·5 + 2·99) \times 5 = 47·45$ per cent. of urea decomposed, therefore phase II = 17·55 per cent.

Estimation of Urea Formed During Hydrolysis of Potassium Cyanate.

Expt. I.—2·025 Grams of potassium cyanate dissolved in 50 c.c. of water ($N/2$) were boiled under reflux for three hours (crystals of ammonium carbonate gradually formed on the sides of the reflux tube), at the end of which time only 1·3 per cent. of the salt remained unchanged. The residue, after the solution was evaporated to dryness at 100°, was extracted with hot alcohol, and the residue from the latter solution, after removal of all ammonium salt, gave, when decomposed with an excess of alkaline solution of sodium hypobromite in the nitrometer, 28·45 c.c. N_2 at 24° and 764 mm. = 25·5 c.c. N_2 at N.T.P., equal to 0·06825 gram of urea = 18·44 per cent., calculated on equation (*b*). The presence of urea was qualitatively proved by its behaviour towards urease, and precipitation as urea nitrate.

Expt. II.—8·1 Grams of potassium cyanate dissolved in 200 c.c. of water ($N/2$) were allowed to remain for ten weeks at the laboratory temperature; 25 c.c. of the solution, after removal of ammonium carbonate, gave 44·09 c.c. N_2 at N.T.P., equal to 62·99 per cent. of urea formed, on basis of equation (*b*).

Expt. III.—0·81 Gram of potassium, 20 c.c. of *N*-sodium hydroxide, and 30 c.c. of water were boiled for three hours in a distillation flask, whilst the concentration was maintained nearly constant. The residual solution gave no nitrogen when tested as above with alkaline sodium hypobromite.

Summary.

(1) The decomposition of urea when heated in aqueous solution in the presence of acids or of alkalis is primarily dependent on its dissociation into ammonia and cyanic acid.

(2) The so-called 'hydrolysis of urea' under such conditions is no more than the hydrolysis of cyanic acid or of an alkali cyanate,

as the case may be, and hence is not a change which gives any support to a 'carbamide' structure, as so commonly suggested.

(3) Under comparable conditions, the velocity of the decomposition of urea is greater in the presence of sodium hydroxide than in the presence of hydrochloric acid, because the proportion of free urea in solution is greater in the former case.

(4) Whilst an ionic theory fails to throw any light either on the conversion of ammonium cyanate into urea or on the formation of urea during the hydrolysis of cyanic acid or of metallic cyanates, it is not in agreement with the facts.

(5) The effect of alcohol in accelerating the transformation of ammonium cyanate into urea and in retarding the decomposition of urea in solution is easily explained by the dissociation theory, with which it is in perfect agreement.

(6) A sterilised solution of urea does not suffer any 'hydrolysis' or reversion to ammonium cyanate at the ordinary temperature. The latter phenomenon can only arise from the dissociation of urea as a preliminary to the change.

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[*Received, October 2nd*, 1917.]

XIV.—*Di*-n-*butylaniline.*

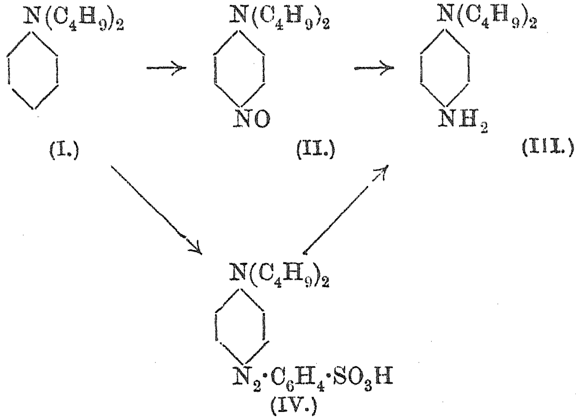
By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

IT has been shown (T., 1917, **111**, 1016) that by heating *n*-butyl chloride and aniline under reflux, *n*-butylaniline is the chief product. This reaction has been further studied, and it has been found that prolonged heating under reflux or the addition of a catalyst such as iodine, favours the production of di-*n*-butylaniline. Its formation was, however, more readily brought about by heating *n*-butyl chloride and aniline under pressure. By heating aniline hydrochloride and *n*-butyl alcohol under pressure, *n*-butylaniline was produced, but this reaction requires a higher temperature and pressure than in the case of *n*-butyl chloride and aniline in order to obtain the same yield.

By repeated fractionation, di-*n*-butylaniline (I) was obtained pure. It was converted into p-*nitrosodi*-n-*butylaniline* (II), which gave additive compounds with certain metallic chlorides.

The nitroso-compound was reduced to p-*phenylenedi*-n-*butyl*-

diamine (III), which, on diazotisation and combination with β-naphthol, furnished *4-di-n-butylaminobenzeneazo-β-naphthol.*



Karrer (*Ber.*, 1915, **48**, 1398), in an attempt to prepare *p*-phenylenedi-*n*-butyldiamine from di-*n*-butylaniline, endeavoured to introduce a *p*-nitroso-group into the dialkylaniline, but was not successful; he states that a nitroso-group cannot be introduced into this compound, and that in this respect it differs from the dipropyl- and lower dialkyl-anilines. We have found, however, that Karrer's statement is incorrect. A nitroso-group can be readily introduced into di-*n*-butylaniline, and this *p*-nitroso-derivative has properties somewhat similar to the lower members of the series, but whilst the latter are solid at the ordinary temperature, *p*-nitrosodi-*n*-butylaniline is an oil. Its constitution was proved by its decomposition into di-*n*-butylamine and *p*-nitrosophenol, almost quantitative yields of which being obtained under certain conditions. It was observed that although *p*-nitroso-*n*-butylaniline was very quickly decomposed by alkali, *p*-nitrosodi-*n*-butylaniline was converted more slowly into the amine and nitroso-compound under similar conditions. Karrer next attempted to prepare *p*-phenylenedi-*n*-butyldiamine by another method, namely, to combine diazotised sulphanilic acid with di-*n*-butylaniline, and to reduce the product. He obtained, however, monobutylaminoazobenzenesulphonic acid, which, on reduction, gave *p*-phenylenemonobutyldiamine, and experiments with di*iso*amylaniline gave similar results. Again we obtained different results from those of Karrer. We found that di-*n*-butylaniline combines in quite a normal manner with diazotised sulphanilic acid, yielding *4-di-n-butylaminoazobenzene-4′-sulphonic acid* (IV), which, on reduction, gives *p-phenylenedi-n-butylaniline.* Diazotised sulphanilic acid reacts

also with mono-*n*-butylaniline, yielding 4-n-*butylaminoazobenzene-4′-sulphonic acid*, and this compound, on reduction, gave *p*-phenylene-*n*-butyldiamine. The two azo-derivatives and the corresponding products of reduction have been compared. The sodium salts of the azo-sulphonic acids differ in the ease with which they crystallise, the di-*n*-butylaminoazobenzenesulphonate being more difficult to obtain in the crystalline condition. The amine dihydrochlorides also differ in their solubilities in alcohol. The amines obtained by reducing the azo-compounds were proved to be identical respectively with the products of reduction of *p*-nitrosodi-*n*-butylaniline and of *p*-nitrosomono-*n*-butylaniline. The two amines are also distinguished by means of their colour reactions with nitrous acid and with ferric chloride. There is the possibility that Karrer was working with di*iso*butylaniline, but from a few experiments carried out, indications were obtained that this compound yields a nitroso-derivative and also couples normally with diazotised sulphanilic acid. Another suggestion is that he was working with a mixture of mono- and di-alkylaniline. A mixture of azo-derivatives would thus be produced on treatment with diazotised sulphanilic acid, and on crystallisation of the sodium salts the mono-*n*-butyl derivative would be obtained, which, on reduction, would give *p*-phenylenemono-*n*-butyldiamine.

EXPERIMENTAL.

By heating aniline and *n*-butyl chloride in molecular proportions for thirty-six hours on the water-bath under reflux, the main product of the reaction has been shown to be mono-*n*-butylaniline. There was also a fraction boiling at 250—270°, which has now been examined. For further investigation, more of this fraction was prepared by heating mono-*n*-butylaniline with one molecular proportion of *n*-butyl chloride under reflux for forty-eight hours. The excess of *n*-butyl chloride was distilled off and the residue rendered alkaline with sodium hydroxide solution. The oil which separated and the ethereal extract of the whole solution were mixed, the resulting ethereal solution was dried, evaporated, and the residue fractionated. Only a small quantity of distillate was obtained boiling below 255°; the fraction boiling between 255° and 265° was collected and further fractionated, when at 260—263°/767 mm., di-*n*-butylaniline distilled as an almost colourless, refractive liquid, which in bulk had a pale yellow tint.

It was found, by heating aniline and *n*-butyl chloride in an autoclave under a pressure of 5—7 atmospheres, that interaction takes place very rapidly; in an hour a 90—95 per cent. yield of

mono-*n*-butylaniline can be obtained. In one experiment, aniline (40 grams) was heated with *n*-butyl chloride (50 grams) at 130—140° in an autoclave for forty-five minutes. The oil which was obtained after the action of sodium hydroxide and treatment in the usual way had the following percentage composition: aniline (estimated as zinc salt), 5·5; mono-*n*-butylaniline (b. p. 232—250°), 90; di-*n*-butylaniline (b. p. 250—260°), 3·5, with a small residue of higher boiling point. By the action of *n*-butyl chloride on mono-*n*-butylaniline under pressure at 180°, a good yield of di-*n*-butylaniline was obtained. When *n*-butyl alcohol and aniline hydrochloride were heated together under pressure, the temperature rising to 200°, mono- and di-*n*-butylaniline were produced. The longer the period of heating, the greater was the quantity of the di-*n*-butyl derivative obtained. The product contained aniline as well as its mono- and di-substituted derivatives. The aniline was removed by heating the mixture with a slight excess of 20 per cent. zinc chloride solution. After well mixing the paste, the insoluble aniline zincichloride was collected, well pressed, and then washed several times with dry ether. The ethereal washings and filtrate were combined, separated from the aqueous layer, and dried, the ether being removed by distillation and the residual oil fractionated. An analysis was made of the fraction referred to above (b. p. 260—263°/767 mm.):

0·1121 gave 0·3380 CO_2 and 0·1134 H_2O. C=82·23; H=11·24.
0·1560 „ 9·4 c.c. N_2 at 19·5° and 751·1 mm. N=6·95.*
$C_{14}H_{23}N$ requires C=81·89; H=11·29; N=6·82 per cent.

Di-*n*-butylaniline is an almost colourless liquid, lighter than water, which darkens very slowly on keeping; it has a very faint but not unpleasant odour, is miscible in all proportions with alcohol or ether, and is soluble in acids, but practically insoluble in water. When potassium ferrocyanide solution is added to a solution of di-*n*-butylaniline in dilute hydrochloric acid, a white precipitate is obtained which is insoluble in water or ether, and only very sparingly soluble in alcohol. On treatment with fuming sulphuric acid, di-*n*-butylaniline gives a *sulphonic acid*, the *barium* salt of which is readily soluble in water, but practically insoluble in absolute alcohol.

* Using copper oxide in the combustion tube, it was difficult to decompose this compound completely, the nitrogen content appeared to be high and repeated estimations gave varying results. An analysis of the gas collected in the nitrometer in one estimation, after drying showed the presence of 18 per cent. of saturated hydrocarbons, and 82 per cent. of nitrogen. When lead chromate was substituted for copper oxide, these difficulties were overcome.

With concentrated nitric acid in the presence of concentrated sulphuric acid, the base yields a yellow, crystalline *nitro*-compound which crystallises from aqueous alcohol in yellow needles; aqueous potassium hydroxide gives a deep red colour when added to its acetone solution. Di-*n*-butylaniline gives a green compound when heated with benzaldehyde and a small amount of zinc chloride.

*Di-*n*-butylaniline hydrochloride* was prepared by passing a stream of dry hydrogen chloride into a solution of the base in dry ether. On the addition of a further quantity of the base, an oil was precipitated which slowly solidified to clusters of colourless needles. The salt melts indefinitely at 90—105°, and solidifies on cooling to a transparent mass:

0·1095 gave 0·0875 AgCl. Cl = 19·8.

$(C_{14}H_{23}N)_2,3HCl$ requires Cl = 20·5 per cent.

This compound is very readily soluble in alcohol or chloroform, sparingly so in benzene, and insoluble in ether. It is not deliquescent.

The *picrate*, prepared in ethereal solution, crystallises from ether in yellow, rectangular plates melting at 125°. The melting point was depressed to 94—95° by the addition of picric acid.

0·1073 Gram of the picrate was dissolved in alcohol, and the solution was made up to 100 c.c. Of this solution, 5 c.c. required 12·0 c.c. of titanous chloride (1 c.c. = 0·000235 gram $C_6H_3O_7N_3$) for reduction, using Knecht and Hibbert's method.

Found: $C_6H_3O_7N_3$ = 52·6.

$C_{14}H_{23}N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$ = 52·7 per cent.

It is readily soluble in acetone, alcohol, benzene, or chloroform, sparingly so in ether, and practically insoluble in water or light petroleum.

p-*Nitrosodi*-n-*butylaniline*.

Di-*n*-butylaniline was dissolved in an excess of dilute hydrochloric acid, the solution cooled with ice, and a solution of sodium nitrite slowly added as long as any action occurred. The deep reddish-brown solution was repeatedly extracted with ether to remove any phenyl-*n*-butylnitrosoamine which would have been formed if any monobutyl derivative had been present, and then rendered alkaline with ammonia. A green turbidity was produced, and the solution was extracted with ether. After drying the ethereal solution and evaporating the solvent, p-*nitrosodi*-n-*butylaniline* was obtained as a green oil:

0·1465 gave 15·3 c.c. N_2 at 20° and 745·5 mm. N = 11·94.

$C_{14}H_{22}ON_2$ requires N = 11·96 per cent.

A dilute ethereal solution of the crude *p*-nitroso-compound changes on keeping from green to a brownish-yellow colour. On passing hydrogen sulphide into an alcoholic ammoniacal solution of this compound, the solution becomes almost colourless. The reduction with zinc dust and hydrochloric acid is described later. The nitroso-compound condenses with β-naphthol in alcoholic solution to give a purplish-blue solution, which yields a precipitate on the addition of zinc chloride solution. The solution dyes chrome-mordanted wool in greenish-blue shades.

p-Nitrosodi-*n*-butylaniline condenses with gallic acid to yield a deep blue, insoluble powder. 9·7 Grams of the hydrochloride were dissolved in 75 c.c. of absolute alcohol and 3·5 grams of gallic acid added. After heating on a water-bath for two to three hours, the alcohol was distilled off, and the residue evaporated to dryness. On extracting the residue with hot water, a dark blue, insoluble powder was left, the alcoholic solution of which dyed wool a blue colour. Analysis gave N = 5·0, whereas the dibutyl homologue of gallocyanine requires N = 7·1 per cent.

p-*Nitrosodi*-n-*butylaniline Hydrochloride.*

A solution of di-*n*-butylaniline (20 grams) in a mixture of 30 c.c. of concentrated hydrochloric acid and 40 c.c. of water was cooled in a freezing mixture, and a concentrated solution of sodium nitrite added, the temperature not being allowed to rise above 5·0°. The mixture initially became pale red, then a darker red, and after passing through a succession of red shades finally almost black. When a slight excess of nitrous acid was present, the mixture was allowed to remain for two to three hours until it had attained the temperature of the room, when a mass of dark, shining crystals was deposited. The crystals were collected and purified by solution in a small amount of alcohol and precipitation with ether, the *hydrochloride* being obtained in small, greenish-yellow crystals.

0·2657 Gram of the hydrochloride was dissolved in water, the solution rendered slightly acid with hydrochloric acid and made up to 100 c.c. It was freed from air by passing in a stream of carbon dioxide. Ten c.c. were reduced by means of standard titanous chloride, using Knecht and Hibbert's method.

0·02657 Gram, in 10 c.c. of above solution, required 19·6 c.c. of $TiCl_3$ (1 c.c. = 0·000147 gram NO); NO = 10·8:

0·3340 gave 0·1773 AgCl. Cl = 13·13.

$C_{14}H_{22}ON_2,HCl$ requires NO = 11·1; Cl = 13·10 per cent.

The hydrochloride is very readily soluble in alcohol or water and insoluble in ether. An aqueous solution gives a red coloration with

ferric chloride solution, and the further addition of an excess of hydrochloric acid produces a precipitate which becomes tarry after a short time.

p-*Nitrosodi*-n-*butylaniline ferrocyanide* was obtained as a pale yellow powder by the addition of a solution of potassium ferrocyanide to a solution of the nitroso-compound in dilute hydrochloric acid. It was washed well with water, absolute alcohol, and finally with ether:

0·1987 gave 0·0346 Fe_2O_3. Fe = 12·18.

$C_{14}H_{22}ON_2,H_4Fe(CN)_6$ requires Fe = 12·40 per cent.

The compound is insoluble in water, alcohol, or ether.

The *platinichloride* is a yellow powder which, on heating, darkens about 180—190°, shrinks at 213—215°, and decomposes at a slightly higher temperature:

0·1232 gave 0·0267 Pt. Pt = 21·67.

$(C_{14}H_{22}ON_2)_2,H_2PtCl_6$ requires Pt = 22·21 per cent.

It is insoluble in ether, sparingly soluble in water, alcohol, or acetone.

The addition of alcoholic solutions of certain other metallic salts to an alcoholic solution of the nitroso-compound produced deep reddish-brown solutions. Many of these, on keeping over calcium chloride in a vacuum desiccator, deposited crystals which were either dark blue or green with a pronounced metallic lustre. They were only slowly hydrolysed by cold water, but more quickly by hot water. Acids rapidly caused hydrolysis.

The *zincichloride* forms steel-blue crystals, which dry to a red powder, melting and decomposing at 153°:

0·1263 gave 0·0623 AgCl. Cl = 12·2.
0·0571 ,, 0·0156 $ZnSO_4$. Zn = 11·1.

$(C_{14}H_{22}ON_2)_2,ZnCl_2$ requires Cl = 11·7; Zn = 10·8 per cent.

It is readily soluble in acetone or tetrachloroethane, moderately so in ethyl iodide, pyridine, or chloroform, very sparingly so in ether or benzene, and insoluble in water, carbon tetrachloride, or chloroform.

The *cadmichloride* forms stellate clusters of blue, flat prisms with a metallic lustre, which dry to a red powder. It does not melt at 260°, although at a considerably lower temperature it softens and darkens somewhat in colour:

0·1039 gave 0·0723 AgCl. Cl = 17·2.
0·0580 ,, 0·0288 $CdSO_4$. Cd = 26·8.

$C_{14}H_{22}ON_2,CdCl_2$ requires Cl = 17·0; Cd = 26·9 per cent.

It is moderately soluble in tetrachloroethane, sparingly so in absolute alcohol or acetone, and almost insoluble in benzene, ether,

light petroleum, or ethyl iodide. It dissolves in pyridine, but there was apparently some change in the compound, for the pyridine solution, on cooling, deposited a yellow solid.

The *mercurichloride* was obtained as a dark green, viscid solid by evaporating an alcoholic solution of mercuric chloride and *p*-nitrosodi-*n*-butylaniline. Benzene was added to precipitate the salt and to dissolve any excess of nitroso-compound.

After being washed several times with dry benzene, the compound was dried in a vacuum desiccator, when it was obtained as an almost black, brittle mass:

0·1373 gave 0·0827 AgCl. Cl=14·9.

$C_{14}H_{22}ON_2,HgCl_2$ requires Cl=14·0 per cent.

It is soluble in tetrachloroethane, acetone, nitrobenzene, chloroform, pyridine, or absolute alcohol, but practically insoluble in water, ether, benzene, or carbon tetrachloride.

The *cuprichloride* crystallises from an alcoholic solution of its components in fine, dark green needles having a decided metallic lustre, softening at 119—120°, and melting and decomposing at 123—125°. On sudden heating, it decomposes with a feeble explosion:

0·0914 gave 0·0446 AgCl. Cl=12·1.
0·0686 ,, 0·0091 CuO. Cu=10·6.

$(C_{14}H_{22}ON_2)_2,CuCl_2$ requires Cl=11·8; Cu=10·5 per cent.

The compound is very readily soluble in tetrachloroethane, and moderately so in chloroform, nitrobenzene, absolute alcohol, or ethyl iodide, giving reddish-brown solutions. In pyridine it dissolves to give a green solution. It is almost insoluble in ether, benzene, carbon tetrachloride, or light petroleum.

On mixing alcoholic solutions of ferric chloride and *p*-nitrosodi-*n*-butylaniline either a pale brown powder or an almost black, amorphous compound was obtained, according to the conditions. The iron derivative apparently had a varying composition. The black precipitate gave Fe=14·7, whilst $C_{14}H_{22}ON_2,FeCl_3$ requires Fe=14·1 per cent. It is insoluble in ether, alcohol, or benzene, and soluble in tetrachloroethane or acetone. The brown precipitate contained Cl=19·7.

The manganous chloride compound was obtained as a very hard, brittle mass by the evaporation in a vacuum of an alcoholic solution of its components. Stannic chloride, nickel nitrate, cobalt nitrate, or cupric nitrate also gave deep brown-coloured solutions when treated under similar conditions, whilst mercuric nitrate gave a precipitate.

Decomposition of p-*Nitrosodi*-n-*butylaniline with Alkali.*

p-Nitrosodi-*n*-butylaniline (9·4 grams) was heated under reflux for four hours with a solution of sodium hydroxide (25 grams) in 600 c.c. of water. The alkaline mixture was then distilled in a current of steam, the distillate being collected in an excess of dilute hydrochloric acid. As soon as the distillate showed absence of alkalinity, the operation was stopped, and the residue in the flask quickly cooled and filtered from tarry matter. It was neutralised by means of sulphuric acid, and extracted with ether several times. On evaporating the ethereal layer, a pale brown solid remained, which was purified by dissolving it in ammonia, passing carbon dioxide through the solution, and extracting with ether. By this means a very faint buff-coloured solid was obtained (m. p. 126—127°), which had the properties of *p*-nitrosophenol, and was characterised by means of its green potassium salt. (Found, K = 24·70. Calc., K = 24·26 per cent.) The hydrochloric acid solution in which the distillate had been collected was evaporated to dryness, leaving an almost white solid, which crystallised from absolute alcohol in white plates. It had the properties of a hydrochloride of a secondary amine and was identified as di-*n*-butylamine hydrochloride. (Found, Cl = 21·43. Calc., Cl = 21·40 per cent.) It was found that the decomposition of *p*-nitroso-*n*-butylaniline was fairly rapid, whilst in the case of the di-*n*-butyl compound the action was much slower. By using an excess of a 10 per cent. solution of sodium hydroxide and heating *p*-nitrosodi-*n*-butylaniline hydrochloride for three hours under reflux before distilling in steam, an almost theoretical yield of the dialkylamine was obtained in the form of its hydrochloride.

We have compared this method of obtaining di-*n*-butylamine with several of the methods employed for the production of the higher alkylamines, as, for example, Chancel's method (*Bull. Soc. chim.*, 1892, [iii], **7**, 405) by heating the alkyl chloride with ammonia, or Berg's method (*Ann. Chim. Phys.*, 1894, [vii], **3**, 392) by heating at 120° a mixture of the alkyl chloride, ammonia, and alcohol. By these methods it is difficult to obtain a compound free from contamination with the monoalkylamine. By the decomposition of *p*-nitrosodi-*n*-butylaniline this difficulty does not arise, and the dialkylamine hydrochloride can be readily obtained in a pure condition.

p-*Phenylenedi*-n-*butyldiamine Dihydrochloride.*

This derivative was prepared by adding an excess of zinc dust gradually to a solution of *p*-nitrosodi-*n*-butylaniline in hydro-

chloric acid. When the zinc had been added the mixture was heated for half an hour on the water-bath, by which time the solution had become almost colourless. The excess of zinc dust was collected and washed well with a small amount of warm dilute hydrochloric acid. The filtrate was treated with sodium hydroxide solution until all the precipitated zinc hydroxide had redissolved, and the separated oil was then extracted with ether. To the washed and dried ethereal solution, a solution of hydrogen chloride in *n*-butyl alcohol was added, when the dihydrochloride was precipitated as a white powder. It was collected, dried at 100°, and purified by dissolving in absolute alcohol and then adding ether, when the hydrochloride was obtained in flocculent masses of white, hair-like crystals. It separated from hot absolute alcohol in white needles:

0·1207 gave 10·25 c.c. N_2 at 18·3° and 737·8 mm. N=9·69.
0·2284 „ 0·2236 AgCl. Cl=24·22.
$C_{14}H_{24}N_2,2HCl$ requires N=9·56; Cl=24·19 per cent.

p-*Phenylenedi*-n-*butyldiamine dihydrochloride* is soluble in water or absolute alcohol, but insoluble in ether. Ferric chloride solution, when added to a neutral solution of the hydrochloride, produces a red coloration, which becomes darker and, after passing through a succession of colours, the solution is finally coloured green. The addition of a small quantity of ferric chloride solution to a solution of *p*-phenylenedi-*n*-butyldiamine dihydrochloride containing hydrogen peroxide produces initially a red colour, which changes to brown and finally becomes colourless. Bleaching powder, dilute bromine water, or neutral potassium dichromate also give a red coloration, which becomes darker, changing to purple. An excess of potassium ferrocyanide produces a red colour which is changed to green by alkalis, and pale green or blue by acids. On warming with potassium dichromate and dilute sulphuric acid or with an excess of ferric chloride, a pungent odour similar to that of *p*-benzoquinone is obtained. A bluish-green thiazine dye was prepared from an aqueous solution of the dihydrochloride by the action of potassium chromate in the presence of di-*n*-butylaniline and sodium thiosulphate. A green dye was also produced by oxidising molecular proportions of di-*n*-butylaniline and *p*-phenylenedi-*n*-butyldiamine hydrochloride. The free *base* is a liquid at the ordinary temperature.

4-*Di*-n-*butylaminobenzeneazo*-β-*naphthol*.

On diazotising *p*-phenylenedi-*n*-butyldiamine hydrochloride (1 mol.) with sodium nitrite in aqueous solution, the solution was

coloured brown and finally changed to green. The diazotised solution was freed from nitrous acid by means of carbamide and poured into an alkaline solution of β-naphthol (1 mol.). *4-Di-n-butylaminobenzeneazo-β-naphthol* was precipitated as a very dark red, insoluble powder. It crystallised from aqueous alcohol as an almost black powder having a slight metallic lustre:

0·0960 gave 9·6 c.c. N_2 at 20° and 743·5 mm. N=11·40.

$C_{24}H_{29}ON_3$ requires N=11·20 per cent.

Concentrated sulphuric acid dissolves this azo-compound, giving a very deep red solution. It is soluble in most organic solvents, but insoluble in water or alkalis. With aqueous platinic chloride the solution of the diazonium chloride gives a pale yellow precipitate which quickly oxidises. The acetylacetone azo-compound was obtained as an orange-yellow precipitate on adding an aqueous solution of the diazonium chloride to an alcoholic solution of acetylacetone in the presence of sodium acetate. β-Naphthylamine also combined with the diazonium chloride, giving a dark red azo-compound. With 2-naphthol-6:8-disulphonic acid ('G' acid) and 8-amino-1-naphthol-3:6-disulphonic acid ('H' acid) it gave dark red dyes.

Combination of Di-n-butylaniline with Diazotised Sulphanilic Acid.

Ten grams of sulphanilic acid were diazotised in the usual way, the solution was freed from any traces of nitrous acid by the addition of carbamide, and gradually added with continuous stirring to a solution of 10 grams of di-*n*-butylaniline in 30 grams of glacial acetic acid, following Karrer's procedure. The acetic acid solution became blood-red and a dark, oily substance separated. When all the diazo-solution had been added, the red solution was left for two hours in a shaker, at the end of which time the solution was removed and the bottle washed out with 100 c.c. of water. On rendering strongly alkaline, the sodium salt separated and was collected. For analysis a portion of the sodium salt was repeatedly extracted with hot absolute alcohol and then crystallised from aqueous alcohol (80 per cent.):

0·1399 gave 0·0239 Na_2SO_4. Na=5·53

$C_{20}H_{26}O_3N_3SNa$ requires Na=5·59 per cent.

Sodium 4-di-n-butylaminoazobenzene-4′-sulphonate is readily soluble in water, only sparingly so in cold aqueous alcohol (80 per cent.), but more readily so in the hot solvent.

The *potassium* salt was also prepared by adding an excess of potassium hydroxide to the red solution (potassium nitrite having

been used in the diazotisation), and purifying in the manner described above:

0·1039 gave 0·2154 CO_2 and 0·0576 H_2O. C=56·54; H=6·16.

0·1857 required 6·34 c.c. $N/5$-H_2SO_4 to neutralise NH_3 (Kjeldahl). N=9·56.

0·1018 gave 0·0204 K_2SO_4. K=9·0.

0·2571 ,, 0·1430 $BaSO_4$. S=7·64.

$C_{20}H_{26}O_3N_3SK$ requires C=56·16; H=6·13; N=9·83; S=7·50; K=9·15 per cent.

It crystallised from aqueous alcohol in small, orange-coloured plates, and was more easily obtained crystalline than the corresponding sodium salt, which it resembled in properties. The free azo-sulphonic acid was obtained by passing dry hydrogen chloride over the dry sodium salt. The mass became very dark red, and when the sodium salt had been completely decomposed the product was extracted several times with small amounts of absolute alcohol. On adding water and allowing to remain for some time, the acid crystallised in small, blue, shimmering cubic crystals, which did not melt at 200°. It was insoluble in benzene or ether, sparingly soluble in water, and readily so in acetone, glacial acetic acid, or absolute alcohol.

*Reduction of 4-Di-*n*-butylaminoazobenzene-4′-sulphonic Acid.*

The sodium salt of the azo-compound was dissolved in water, the solution acidified with hydrochloric acid, and reduced by gradually adding an excess of zinc dust. The solution became hot and soon decolorised. After heating on a steam-bath, the excess of zinc dust was filtered off and the filtrate evaporated to about half its bulk. After adding a concentrated solution of sodium hydroxide until all the precipitated zinc hydroxide had dissolved, the whole was extracted with ether, the ethereal solution dried, and a solution of dry hydrogen chloride in butyl alcohol added, when a white precipitate was formed, which proved to be identical with *p*-phenylenedi-*n*-butyldiamine dihydrochloride. (Found, Cl=24·4. Calc., Cl=24·2 per cent.)

*Sodium 4-Mono-*n*-butylaminoazobenzene-4′-sulphonate.*

To a solution of mono-*n*-butylaniline (4 grams) in glacial acetic acid (15 grams) a diazotised solution of sulphanilic acid (5 grams) was slowly added with continual stirring, following the procedure described previously. The liquid became deep brownish-red, but after shaking for four hours the colour had changed to a very deep red. The red solution was poured off, and some separated solid

matter extracted with dilute sodium hydroxide, the extract being added to the main bulk of the liquid. On rendering slightly alkaline by the addition of concentrated sodium hydroxide solution and keeping the mixture cooled in ice, a pale orange-yellow precipitate was obtained, which, after half an hour, was collected and dried. For analysis a portion was extracted with absolute alcohol several times, and finally crystallised twice from aqueous alcohol:

0·1063 gave 0·2106 CO_2 and 0·0505 H_2O. C=54·03; H=5·28.

0·1758 „ 18·1 c.c. N_2 at 20·7° and 757 mm. N=11·92.

0·1489 „ 0·0293 Na_2SO_4. Na=6·37.

$C_{16}H_{18}O_3N_3SNa$ requires C=54·06; H=5·11; N=11·83; Na=6·47 per cent.

The sodium derivative crystallised in small, flocculent masses, soluble in water, but sparingly so in absolute alcohol. This compound was more easily obtained crystalline than the sodium salt of dibutylaminoazobenzenesulphonic acid.

*Sodium 4-mono-*n*-butylaminoazobenzene-4′-sulphonate* was reduced by means of zinc dust and hydrochloric acid. After filtering off the excess of zinc dust and rendering strongly alkaline with sodium hydroxide solution, the solution was extracted with ether. The addition of alcoholic hydrogen chloride to the ethereal extract gave a white precipitate which crystallised from alcohol in white, shining plates, and was identified as *p*-phenylenemono-*n*-butyldiamine dihydrochloride. (Found, Cl=29·98. Calc., Cl=29·90 per cent.) On rendering alkaline, *p*-phenylenemono-*n*-butyldiamine was obtained on extraction with ether in white, glistening plates melting at 31° (T., 1917, **111**, 1033). After crystallisation from light petroleum, a mixture with a specimen of the base obtained by the reduction of *p*-nitroso-*n*-butylaniline melted at the same temperature.

[*Received, December 6th*, **1917.**]

XV.—*Studies of Drying Oils. Part I. The Properties of some Cerium Salts obtained from Drying Oils.*

By Robert Selby Morrell.

Cerous salts of a number of organic acids have been described by Rimbach and Kilian (*Annalen*, 1909, **368**, 110), Morgan and Cahen (T., 1907, **91**, 477), Biltz (*Zeitsch. anorg. Chem.*, 1905, **45**,

89; *Annalen*, 1904, **331**, 334), and Levy ("Chemistry of the Rare Earths," 134).

The autoxidation of the cerous compounds has been investigated by Baur (*Zeitsch. anorg. Chem.*, 1897, **13**, 251; *Ber.*, 1903, **36**, 2658), Job (*Ann. Chim. Phys.*, 1900, [vii], **20**, 205), and Engler (*Ber.*, 1902, **35**, 2642), and the catalytic activity of the ceric and cerous salts has been discussed by Barbieri (*Atti R. Accad. Lincei*, 1907, [v], **15**, i, 395, 399).

In view of the large proportion of cerite earths in monazite sand it seemed advisable to investigate the properties of cerous and ceric salts of aliphatic acids of the C_{16} and C_{18} series, with special reference to their solubility in solvents and to the catalytic activity of the contained metal.

The general methods of preparation of cerous salts of organic acids are:

(1) By the action of acid on freshly precipitated cerous carbonate.

(2) By the interaction of a soluble cerous salt and the potassium salt of the corresponding acid.

The first method leads to the formation of acid salts of the type X3Ce,X, the second to the production of salts of the normal type, CeX3 (Rimbach and Kilian, *loc. cit.*) [X = acidic radicle].

In this paper the cerous salts of the following acids have been prepared and their properties investigated: palmitic, stearic, oleic, elaidic, linoleic, α- and β-elæostearic, linolenic, and abietic acids.

The method of preparation of the normal salts has been employed, and it must be pointed out that special precautions must be taken to ensure satisfactory neutralisation, otherwise the precipitated salts may be contaminated with excess of either acid or cerium.

All the salts are colourless and insoluble in water.

Cerous stearate, elaidate, β-elæostearate, and palmitate are insoluble in ether. When freshly prepared, cerous oleate, linoleate, linolenate, α-elæostearate, and abietate are readily soluble in ether or turpentine. Cerous palmitate and stearate, like the corresponding lead salts, are insoluble in turpentine.

No suitable solvents could be found from which the salts could be satisfactorily crystallised. In the case of acids forming cerous salts insoluble in ether, the granular precipitate was analysed directly, but where the salt was soluble the ethereal solution was concentrated and the solid salt obtained thereby was analysed. In all cases the salts were of the normal type CeX_3.

The ethereal solutions of the cerous salts of the unsaturated acids darken on keeping or on exposure to air and, in the case of the

linolenate, a buff-coloured precipitate having a peroxide reaction separates, corresponding with $CeO(XO_2)_2$, basic ceric oxylinolenate, and the brown ethereal solution would appear to contain a mixture of CeX_3 and CeX_4 or $CeX_3 + 5O_2 = 2CeO(XO_2)_2 + 2CeX_4$.*

Cerous oleate in ether gives, on exposure, a slight turbidity, and the solution changes only slightly towards the dark brown colour of ethereal cerous and ceric linolenates.

In an investigation of the changes which occur when drying oils are polymerised by heat (Morrell, *J. Soc. Chem. Ind.*, 1915, **34**, 105), it was pointed out that there was evidence of the shifting of intramolecular linkings prior to polymerisation.

The marked differences with regard to the insolubility in ether between cerous oleate and elaidate and cerous α- and β-elæostearates suggested that differences might be observed in the cerous salts obtained from the various thickened oils, which would give further support to the idea of change of linking.

From olive oil were obtained cerous salts of the normal type CeX_3, soluble in ether and passing only slowly into an insoluble, $CeOX_2$, type. When the olive oil is heated out of contact with the air (Morrell, *loc. cit.*), part of it (barium salt insoluble in ether or a mixture of benzene and alcohol) is of the normal type, but the barium salt soluble in a mixture of benzene and alcohol gives a soluble salt of the CeX_4 type and an insoluble basic ceric salt, $CeOX_2$. The olive oil underwent no polymerisation during the heating.

From poppy-seed oil, heated under the same conditions and containing no polymerised compound, similar cerium salts of the types CeX_4 and $CeOX_2$ were obtained. The original poppy-seed oil gave a salt of the normal CeX_3 type.

From thickened linseed oil after the removal of the polymerised substance by means of acetone the yield of basic ceric salt, $CeOX_2$, increased to nearly 50 per cent. A blank experiment with untreated linseed oil gave the normal CeX_3 and only 12·4 per cent. of a ceric salt of the $CeO(XO_2)_2$ or $CeO(XO_4)_2$ type.

The results of these experiments do not indicate conclusively that changes in linking have occurred, although full precautions were taken to avoid oxidation during the heating of the oils and in the preparation of the cerium salts. The probability of oxidation is too great to be ignored; nevertheless, in olive oil the presence of two glyceride modifications is indicated; one yielding, after heating, the normal type of cerium salt, whilst the second gives an oxidised type of cerium salt showing the existence in the oil of

* On free exposure to air, an insoluble salt of the type $CeO[XO_4]_2$ was obtained.

modifications with different properties. Applying this view to poppy-seed and linseed oil and with due consideration to chances of oxidation and formation of mixed cerium salts, there remain grounds for belief that during the thickening of poppy-seed and linseed oil changes of linking occur with the formation of modifications which on continued heating out of contact with air are polymerisable.

The properties of the cerium salts from thickened linseed oil (soluble in acetone), on the whole, resemble those from thickened poppy-seed oil, which is to be expected as the linolenic glyceride has been removed from the linseed oil by acetone after the thickening.

It seemed advisable to investigate the cause of the change in solubility without change in colour observed in certain cerium salts (for example, cerous α-elæostearate) after treatment with ether. Since the possibility of oxidation could not be decided by a cerium estimation, cerium α-elæostearate was transformed into the corresponding acid, which was examined for evidences of oxidation.

The experimental difficulties lie in the fact that China wood oil, in addition to small quantities of oleic acid and β-elæostearic acid, often contains oxidised acids, as shown by the liberation of iodine from potassium iodide: in marked contrast to linseed oil, which liberates comparatively a smaller amount of iodine.

It was found that the freshly prepared salt, readily soluble in ether, gave an acid with the melting point and high iodine value of α-elæostearic acid, but the salt, formerly soluble, and afterwards insoluble in ether, yielded a mixture of a crystalline acid melting at 45—46° and having an iodine value of 177·8, and a syrupy acid with a lower iodine value and varying iodine-liberation value.

Lead α-elæostearate was found to give 25 per cent. of a salt soluble in ether, containing an oxidised acid, and the insoluble part furnished a good yield of an acid melting at 44°.

The conclusion drawn from the experiments is that partial oxidations have occurred in spite of all precautions taken, although the cerium α-salt in ethereal solution gave no precipitate when air or oxygen was passed through it.

The occurrence of mixed unoxidised and oxidised acid in the insoluble salt can only be accounted for by the formation of an insoluble basic ceric salt of the type Ce_2X_6O (Ce = 14·1) and subsequent partial oxidation of the acid, although no decided colour change characteristic of ceric salts was observed. No appreciable amount of β-elæostearic acid was identified, so that stereoisomeric change had not occurred. If this is not admitted, then a change in the form of the cerium salt must have occurred without the pro-

duction of isomerism in the acid radicle. The evidence, on the whole, supports the theory of the formation of a basic ceric salt with subsequent partial oxidation of the acid radicle.

The rate of absorption of oxygen by cerous α-elæostearate shewed that half the amount of oxygen was absorbed in the first day, whilst more than ten days were required before the salt became approximately constant in weight.

The study of the oxygen absorption of the salt was easy to follow, and showed that with the formation of a basic ceric α-elæostearate of the type $Ce_2O(XO_2)_6$, from CeX_3 or Ce_2X_6O, one molecule of oxygen per molecule of acid was absorbed or that only one double linking was affected, so that the iodine value and the iodine-liberation value became approximately equal. It was only after a year's exposure to oxygen that the second double linking of elæostearic acid was peroxidised.

The peroxidic acid showed gradual polymerisation until the syrupy acid set to a varnish. It had all the properties of peroxidic acids described by Harries, namely, instability in the presence of alkalis, but stability towards dilute acids, and was not reduced by zinc dust and acetic acid.

The investigation of these peroxidic acids will be continued because the study of them will go far to elucidate the problem of drying oils.

Another interesting result was the indication of the presence of the β-acid among the products of oxidation of cerous α-elæostearate. β-Elæostearic acid is less easily oxidised than the α-modification, and can be separated from the mixed acids, as it is soluble in light petroleum whilst the peroxidic acid is insoluble. The yield of the acid is small, not more than 10 per cent., and, moreover, its potassium salt is comparatively stable in air. At present it must be regarded as a component of the sample of the original oil, although its cerium salt is sparingly soluble in ether and only the salt soluble in ether was employed.

The change of the α-glyceride into the β-glyceride has already been investigated (Morrell, T., 1912, **101**, 2082), and in a later communication the transformation of the α-methyl ester into the β-ester will be described.

From the results stated, the author is inclined to consider that, in drying oils, oxidation to peroxidic acids is followed by polymerisation. This polymerisation may be accelerated by other agents, which would account for a common practical use of two different driers, one essential for oxidation and the other for accelerating the subsequent polymerisation.

The oxidation of cerium α-elæostearate shows that its function as a drier can be represented by the following scheme:

$$CeX_3 \text{ or } Ce_2OX_6 \longrightarrow Ce_2(XO_2)_6$$

$$Ce_2O(XO_3)_6 + \text{drying oil} \longrightarrow CeX_3 + \begin{matrix} O\cdot CHY \\ | \\ O\cdot CHZ \end{matrix} \text{ [oxidised oil.]}$$

From evidence given before, especially under cerous linolenate, it is probable that the cerium assumes the ceric state, but it must be pointed out that the colour changes are not very marked, as would be expected if a ceric salt were formed. This may support the view of the transient nature of the ceric form.

The above representation agrees with the views of Ingle (*J. Soc. Chem. Ind.*, 1917, **36**, 318) for lead linolenate. The action of cerium salts as driers has been investigated by the author several years ago. It was found that cerium linoleate from linseed oil was a more active drier than lead linoleate, but inferior to manganese and cobalt linoleates (Mackay and Ingle, *J. Soc. Chem. Ind.*, 1917, **36**, 318).

The addition of a cerium drier to a varnish containing a lead drier does not accelerate the time of drying like a cobalt or manganese linoleate. It was observed that within a limiting value of cerium content the time of drying of a standard varnish under works conditions was independent of the mass of the cerium present.

This result is what would be expected from theory.

It is the intention of the author to investigate further the cerium salts of the acids from drying oils, and it is solely due to the pressure of war work that the results are submitted for publication in an incomplete form, but they are, in the author's opinion, of sufficient importance to justify the course taken.

EXPERIMENTAL.

Cerous Stearate.—This salt was prepared from pure stearic acid and pure cerous nitrate, the precipitation being carried out in neutral or slightly acid solution. It is a white, granular salt insoluble in water and very sparingly soluble in ether (0·6 per cent.) or cold turpentine; in these respects it resembles lead stearate. For analysis it was purified by means of ether:

1·0000 gave 0·1710 CeO_2. Ce = 13·91.

$(C_{18}H_{35}O_2)_3Ce$ requires Ce = 14·20 per cent.

Cerous Palmitate.—Cerous palmitate was prepared in the same manner from palmitic acid (Kahlbaum), and is a white, insoluble, granular salt. In ether its solubility is 0·8 and in turpentine 0·18

per cent. The solubility of lead palmitate in turpentine at 15° is 0·106 per cent.:

0·7544 (dried in a vacuum) gave 0·1418 CeO_2. Ce=15·3.
0·5540 (extracted with ether) gave 0·108 CeO_2. Ce=15·87.

$(C_{16}H_{31}O_2)_3Ce$ requires Ce=15·36 per cent.

Cerous Oleate.—Cerous oleate (compare Morgan and Cahen, *Pharm. J.*, 1907, **78**, 428), prepared from oleic acid (Kahlbaum), is a white, granular solid which is completely soluble in ether. The ethereal solution can be kept for months in a bottle in the dark without precipitation, only a slight browning of the solution being observed:

0·8180 (dried in a vacuum) gave 0·148 CeO_2. Ce=14·73.
0·8928 (from olive oil) gave 0·1582 CeO_2. Ce=14·13.*

$(C_{18}H_{33}O_2)_3Ce$ requires Ce=14·24 per cent.

The high values of cerium in the analyses are due to the slight alkalinity of the solution from which the cerium salt was precipitated.

Cerous Elaidate.—This salt is obtained in the usual manner, but it is precipitated slowly and in a more finely divided state than the oleate. Its solubility in ether is 1·07 per cent.:

0·9678 gave 0·1744 CeO_2. Ce=14·66.

$(C_{18}H_{33}O_2)_3Ce$ requires Ce=14·25 per cent.

Cerous Linoleate.—Linoleic acid was prepared from the corresponding tetrabromide (Rollett, *Zeitsch. physiol. Chem.*, 1909, **62**, 410). It had an iodine value of 179·6 (Wijs).

A solution of pure cerous nitrate was added to a carefully neutralised solution of linoleic acid, and the white, granular precipitated salt was analysed after being dried in a vacuum:

1·2304 gave 0·221 CeO_2. Ce=14·62.

The salt was extracted with ether, in which it was completely soluble, and on evaporation of the filtered solution the dried salt was analysed:

0·9940 gave 0·1790 CeO_2. Ce=14·66.

$(C_{18}H_{31}O_2)_3Ce$ requires Ce=14·33 per cent.

Cerium α-Elaeostearate.—The salt was prepared from Chinese wood oil by saponification in the cold, neutralisation by acetic acid (cerous acetate is soluble in water), and addition of an aqueous solution of cerous nitrate.

The freshly prepared salt is completely soluble in ether, but if dried out of contact with air it is no longer soluble in that medium.

An analysis of the freshly precipitated salt (which furnished an

* A third analysis gave Ce=14·85.

acid melting at 45—46°; I.V.=177·8) gave the following numbers:

1·1060 gave 0·198 CeO_2. Ce=14·64.*

$(C_{18}H_{31}O_2)_3Ce$ requires Ce=14·34 per cent.

The salt purified by solution in ether and subsequent removal of the solvent in a current of coal gas contained Ce=14·56, and gave an acid melting at 44—45°.

On further examination it was found to be no longer completely soluble in ether, which fact points to either oxidation during drying or to some isomeric change.

Precautions were taken to exclude oxygen during the drying, although it must be admitted that oxygen combines readily with the salt.

An analysis of a quantity of the salt which had been dried in a vacuum and kept for some time in a sealed tube in the dark showed only a slight fall in the cerium content, but 86 per cent. of the salt was found to be insoluble in ether. The slight fall in the cerium content would be accounted for by unavoidable oxidation during the drying of a larger quantity of the salt:

1·1230 gave 0·1900 CeO_2. Ce=13·77.

The acid obtained from the cerium salt insoluble in ether was an oil [I.V.=88 (Wijs)] liberating 28·9 per cent. of iodine, and having a molecular weight in glacial acetic acid of 411·9. It reduced Fehling's solution and restored the colour to bleached magenta solution. The slight fall in the cerium content indicates considerable modification in the acid, which would appear to have become partly oxidised and gradually polymerised to a substance, $(C_{18}H_{32}O_2,O_2)_y$.

Lead α-elaeostearate was prepared in the usual manner from cold hydrolysed wood oil.

Found: Pb=27·12. $(C_{18}H_{31}O_2)_2Pb$ requires Pb=27·06 per cent.

From the lead salt the corresponding acid was obtained which, on crystallisation from alcohol, melted at 48·5°. The acid liberated in two hours only 7·52 per cent. of iodine from potassium iodide in acetic acid solution. It was found that 73·4 per cent. of the original salt was insoluble in ether, and from it an acid was obtained melting at 44—45°. In its insolubility in ether lead α-elæostearate is markedly different from the cerous salt.

The portion of the soluble salt was found on recovery to be only partly soluble in the solvent, and the permanently soluble portion furnished an oily acid with an iodine value of 104 after one and a-half hours and 115 after twenty-two hours (Wijs) and liberated 36·59 per cent. of iodine after one hour.

* A second analysis gave Ce=14·25.

The oxidation of cerium α-elæostearate will be described in detail later.

Cerous β-Elaeostearate.—β-Elæostearic acid (Morrell, T., 1912, **101**, 2082) was neutralised with the calculated quantity of potassium hydroxide and the potassium salt was dissolved in hot water (5·734 grams required 800 c.c. of hot water for complete solution). With aqueous cerium nitrate a white, granular precipitate was obtained. It is very sparingly soluble in ether or other organic solvents with the exception of hot benzene, from which it can be obtained as a white powder on evaporation of the solvent. The salt can be dried in a vacuum at 110° without loss in weight:

1·0436 gave 0·1526 CeO_2. Ce = 14·25.

$(C_{18}H_{31}O_2)_3Ce$ requires Ce = 14·34 per cent.

It must be pointed out that special precautions must be taken in the precipitation of the salt so as to ensure a neutral solution. Unless care be taken, the cerium content in the precipitated salt may fall to 13·6.

After recrystallisation from acetone, β-elæostearic acid showed an iodine-liberation value of 0·8 per cent. of iodine (two hours). On exposure in the dark in dry air for a fortnight it gained nothing in weight, although there was a faint, rancid odour, but no change in colour. In the light the gain in weight after a month was 2·3 per cent. The potassium salt of the β-acid, on exposure to air in fourteen days, gained only 0·22 per cent. in weight, and after a month's exposure in light the gain in weight was 1·22 per cent., although the salt had become slightly yellow.

Cerous Linolenate.—Kahlbaum's linolenic acid (iodine value, 276—279) and pure cerous chloride were used for the preparation of the salt. Cerous linolenate is a white, granular solid which is completely soluble in ether. The ethereal solution was evaporated in a coal-gas atmosphere and the salt dried in a vacuum. It did not show as great a tendency to pass into an insoluble form as in the case of cerous α-elæostearate, and the salt can be kept for a month in a sealed tube without losing its power of dissolving in ether:

0·8098 gave 0·1480 CeO_2. Ce = 14·7.

$(C_{18}H_{23}O_2)_3Ce$ requires Ce = 14·42 per cent.

The ethereal solution of the salt gradually darkens in colour when exposed to light and a brownish-buff-coloured precipitate is formed, which liberates iodine from potassium iodide in dilute acetic acid solution. It is presumably a basic ceric salt of an oxylinolenic acid:

0·0804 gave 0·0184 CeO_2. Ce = 18·63.

$CeO(C_{18}H_{29}O_2)_2$ requires Ce = 19·7 per cent.

$CeO(C_{18}H_{29}O_2,O_2)_2$ requires Ce = 18·10 per cent.

On free exposure to air, the ethereal solution deposited a salt [Ce=17·0]. $CeO(C_{18}H_{29}O_2,O_4)_2$ requires Ce=16·7, and $CeO(C_{18}H_{29}O_2,3O)$ requires Ce=17·3 per cent. The brown-coloured ethereal solution contained a cerium salt:

0·9356 gave 0·1484 CeO_2. Ce=12·91.

Most probably the brown ethereal solution contained a mixture of ceric and cerous salts of the types CeX_4 (Ce=11·2) and CeX_3 (Ce=14·4), rather than a basic ceric oxylinolenate of the type $Ce_2O(XO_2)_6$ (Ce=13·0 per cent.). The proportion of oxidised insoluble salt to oxidised soluble salt was 1:5·2.

The change of colour to a yellow or brown shade is noticeable when solutions of cerous salts in organic solvents are exposed to the air.

Reference will be made to the other basic salts in the examination of ceric salts from drying oils.

Cerous Abietate.—Abietic acid was prepared from French rosin by repeated recrystallisation from 70—90 per cent. alcohol. On the ninth crystallisation an acid was obtained melting at 150—156°. The white cerous abietate dissolves in ether to the extent of 97·8 per cent., is soluble in turpentine, and does not lose weight at 100—110°:

0·9772 gave 0·163 CeO_2. Ce=13·62.

$(C_{20}H_{29}O_2)_3Ce$ requires Ce=13·43 per cent.

The cerium salt prepared from crude American resin was not completely soluble in ether (15·44 per cent. was insoluble), and it contained only 10·2 per cent. of cerium owing to the presence of abietic anhydride. The cerium salt soluble in ether contained Ce=7·83 per cent.

An ethereal solution of cerous abietate gradually becomes orange and a precipitate is formed, similar to the behaviour of cerous linolenate in ether.

Cerous Salts from Thickened Drying Oils.

Olive Oil.—After the saponification of olive oil, the lead salt soluble in ether was transformed into the barium salt, which was treated with a mixture of benzene and alcohol, whereby 25·9 per cent. dissolved (Morrell, *loc. cit.*). It may be pointed out that 47·8 per cent. of the barium salt soluble in a mixture of benzene and alcohol is soluble in ether.

The cerous salt from the soluble barium salt gave the following result on analysis:

0·8928 gave 0·1582 CeO_2. Ce=14·13.

$(C_{18}H_{33}O_2)_3Ce$ requires Ce=14·24 per cent.

The salt of the CX_3 or normal type is soluble in ether, although on exposure to air it becomes only partly soluble, leaving a residue (30·86 per cent. of the whole), which contains Ce=20·15 and is evidently basic ceric oleate.

$CeO(C_{18}H_{33}O_2)_2$ requires Ce=19·5 per cent.

The cerium salt from the insoluble barium salt is likewise of the normal type.

From the thickened olive oil (Morrell, *loc. cit.*) the barium salt, insoluble in a mixture of benzene and alcohol and insoluble in ether, gave a cerous salt of the normal type soluble in ether:

0·9964 gave 0·166 CeO_2. Ce=14·03.

This salt could be completely redissolved in ether.

On the other hand, the cerium salt from the barium salt (37·2 per cent.) soluble in a mixture of benzene and alcohol was of two types, namely, one soft and viscous, soluble to the extent of 68·45 per cent. in ether and containing Ce=11·62, whereas a salt of the CeX_4 type requires Ce=11·07 per cent., and the other of the basic ceric type $CeOX_2$ containing Ce=19·9 (Calc., Ce=19·5 per cent.).

Thickened Poppy-seed Oil.

The cerous salts of the raw poppy-seed oil are of the normal type, CeX_3, and soluble in ether to the extent of 93 per cent. When poppy-seed oil is thickened (Morrell, *loc. cit.*), two types of cerium salts are obtained from the oil soluble in acetone, namely, CeX_4 (65 per cent.), containing Ce=11·36 per cent. and soluble in ether, and $CeOX_2$ (25 per cent.), containing Ce=20·9 per cent. and insoluble in ether.

From the iodine values of the acids obtained directly from the thickened oil, there is no evidence that oxidation has occurred during heating, but the acid obtained from the cerium salt of the CeX_4 type has an iodine value of 71—79, indicating that oxidation of the cerium had taken place, presumably during the handling of the salt, and it is possible that the salts of the CeX_4 and $CeOX_2$ types may contain partly oxidised X-groups, which would explain the low iodine value given above.

Thickened Linseed Oil.

Ordinary linseed oil was transformed into the lead salt soluble in ether, and from it into barium salts, which were extracted with a warm mixture of benzene and alcohol; of these, 82·5 per cent. consisted of the normal CeX_3 type [soluble in ether, but not completely soluble in that solvent on careful recovery], and the in-

soluble residue showed ceric properties, with 12·4 per cent. of the $CeO(XO_2)_2$ or $CeO(XO_4)_2$ types.

When linseed oil is thickened by heating under the conditions previously referred to, the mixture of cerium salts obtained from the non-polymerised part soluble in acetone is soluble in ether only to the extent of 50 per cent., and consists essentially of salts of the CeX_4 and $CeOX_2$ types (see above). It is difficult to avoid completely chances of oxidation during the thickening of the oil and the handling of the cerium salts, but the results seem to indicate the production of modifications of the oil on heating, which are prone to oxidation, and this view is not contrary to experience with thickened oils as drying oils.

The Oxidation of Cerous α-Elaeostearate.

The absorption of dry oxygen by cerous α-elæostearate, soluble in ether, and recovered from that solvent, was determined by:

(*A*) Direct measurement of the volume of oxygen absorbed.

(*B*) Increase in weight of cerous salt.

(*A*) 0·268 Gram of cerous α-elæostearate, soluble in ether, was kept in contact with a known volume of pure dry oxygen and the diminution in volume observed.

Percentage Weight of Oxygen Absorbed.

In 16 hours at room temperature	4·4
,, 24 ,, ,, ,,	8·7
,, 3 ,, ,, ,,	9·37
,, 4 ,, ,, ,,	9·79

$Ce_2O(C_{18}H_{31}O_2,O_2)_6$ requires 9·66 per cent.
$Ce_2(C_{18}H_{31}O_2,O)_3$ requires 9·8 per cent.

In 4⅔ days at room temperature	10·0
,, 6⅔ ,, ,, ,,	10·8
,, 7⅔ ,, ,, ,,	11·19
,, 16⅔ ,, ,, ,,	12·54
,, 65 ,, ,, ,,	17·43
,, 10 months ,, ,,	19·01

$Ce(C_{18}H_{31}O_2,O_4)_3$ requires 19·65 per cent.
$Ce_2O(C_{18}H_{31}O_2,O_4)_6$ requires 19·3 per cent.

After ten months, the salt gave the following results on analysis:

0·281 gave 0·042 CeO_2. Ce=12·1.

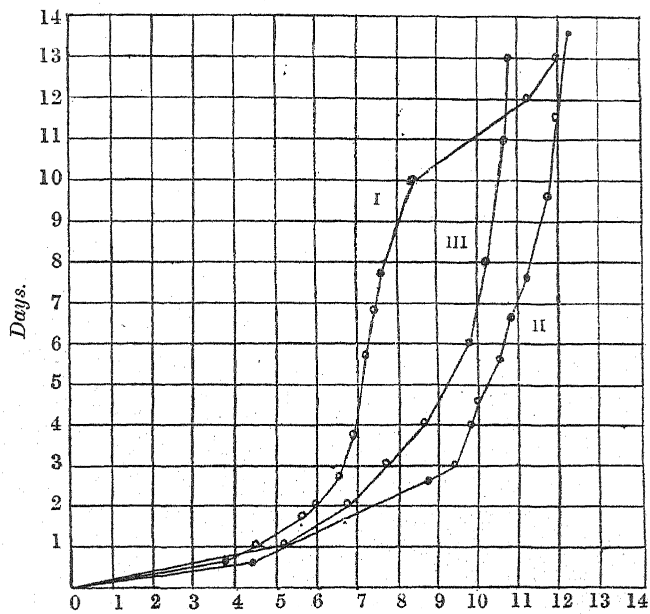
$C_{18}H_{31}O_2,O_4)_3Ce$ requires Ce=11·97 per cent.
$(C_{18}H_{31}O_2,O_4)_3CeO$ requires Ce=11·81 per cent.

(*B*) Quantities of about 20 grams of the salt, purified by ether, were kept in dry oxygen and the gain in weight of the salt was determined from time to time.

		Per cent.	
19·243 Grams showed a gain in weight in	1 day =	6·82	5·27
	3 days =	—	7·7
(Average temperature 120°)	4 ,, =	8·65	—
	6 ,, =	9·8	9·6
	8 ,, =	10·24	—
	11 ,, =	10·66	10·4
	13 ,, =	10·9	0·6

During the first eight hours, the rise in temperature of the salt was very decided, and after five hours the difference in tempera-

Absorption of Oxygen by Cerium Elaeostearate.



Percentage weight of oxygen absorbed.

Curves I and II were obtained from the volume changes of the oxygen. Curve III shows the percentage increase in weight of the salt.

ture between the salt and the air in the room was as great as 11·5°; at the end of eight hours the difference was 3·5°.

The relations between time and absorption are shown in the curves. In curve I, after the tenth day, the salt was repowdered and the oxygen renewed.

The cerium salt, in ethereal solution, was transformed into the acid by means of dilute sulphuric acid, whereby a viscous oil of slight rancid odour was obtained. It was extracted by light petroleum, in which 4 to 14 per cent. was soluble. The part soluble in light petroleum was a syrup, from which crystals melting at 67—68° were obtained. These were presumably β-elæostearic acid.

The syrupy mother liquor had strong reducing and peroxidic properties, and was probably of an aldehydic or aldehydo-acidic character. The residue insoluble in light petroleum was a viscous solid with strong peroxidic properties, which were destroyed on warming the substance with mineral acids or alkalis, but were retained in the presence of 10 per cent. acetic acid. On warming with dilute sulphuric acid and testing with titanium dioxide, a definite peroxidic reaction was obtained:

0·1544 gave 0·3878 CO_2 and 0·1328 H_2O. C=68·5; H=9·56.

0·1370 „ 0·340 CO_2 and 0·1124 H_2O. C=68·48; H=9·11.

Iodine value=79·35; iodine liberated in two hours=50 per cent. O=6·3; in twenty hours=73·63 per cent. O=9·3.

$C_{18}H_{32}O_4$ requires C=69·23; H=10·25 per cent. Iodine value=81·4. O=10·3 per cent. Iodine liberated=81·6 per cent.

$C_{18}H_{32}O_5$ requires C=66·00. H=9·7 per cent. Iodine value=73·4.

The viscous mass undergoes slow polymerisation, and the molecular weight increases when the substances is kept in a vacuum, so that it eventually hardens to a varnish-like mass. In glacial acetic acid (after fourteen days in a vacuum), M.W.=484—518.

After twenty-eight days in a vacuum, M.W.=518—535.

After two months in a vacuum, M.W.=654—691.

$C_{18}H_{32}O_4$ requires M.W.=312.

The peroxidic acid was boiled with freshly prepared calcium carbonate and water under reflux for three hours, and then extracted with ether. The ethereal extract (14·7 per cent.) was a syrup reducing Fehling's solution and having the usual peroxidic properties.

The red, viscous residue, which likewise reduced Fehling's solution, liberated iodine from potassium iodide and gave a hydrogen peroxide reaction with titanic oxide. It yielded a series of viscous salts with soluble barium, cadmium, cobalt, copper, and strontium compounds, and in slightly ammoniacal solution, a granular, basic lead salt of the peroxidic acid:

1·4586 gave 0·8238 $PbSO_4$. Pb=38·61.

$C_{18}H_{31}O_2,O_2,PbOH$ requires Pb=38·69 per cent.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant defraying the cost of the investigation, and to Messrs. Mander Brothers for permission to publish the results.

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[*Received, December 11th, 1917.*]

XVI.—*The Colouring Matters of Camwood, Barwood, and Sanderswood.*

By PAULINE O'NEILL and ARTHUR GEORGE PERKIN.

OF the four well-known "insoluble" red dye-woods, sanderswood, barwood, caliaturwood, and camwood,* the first-named has been most closely examined, and although barwood and caliaturwood have received some attention, no description of the colouring matter of camwood appears to be on record. The close similarity in the dyeing properties of these woods, and the fact that all are substantive to wool, suggests that the dyes present are chemically allied, and it is indeed conceivable from the very similar shades given by sanderswood, barwood, and caliaturwood that the same colouring matter may be present in each case. Camwood, on the other hand, gives with mordanted wool somewhat bluer tones,

	Chromium.	Aluminium.	Tin.	Iron.
Camwood	Reddish-violet	Red	Bluish-red	Violet
Sanderswood	Brownish-red	Orange-red.	Red	Maroon

and its colouring matter, according to dyers, is more readily dissolved by water than that of the other dye-woods of this class. A chemical comparison of this with the santalin of sanderswood appeared desirable, the latter having somewhat recently been closely studied by Cain and Simonsen (T., 1912, **101**, 1061). These authors have suggested for santalin the formula $C_{15}H_{14}O_5$, also considered probable by Weyermann and Haffely (*Annalen*, 1850, **74**, 226), and find that this may be expressed as

$$C_{14}H_9O_2(OH)_2(OMe).$$

Of the numerous derivatives of this colouring matter described in their paper, santalin dimethyl ether, $C_{14}H_9O_2(OMe)_3$, is specially interesting in that, by oxidation, veratric, anisic, and butyric acids can be prepared from it. That sanderswood contains, in addition to santalin, a second colouring matter appears possible from the work of Weidel (*Zeitsch. für Chem.*, 1870, **6**, 83), who obtained from it, in addition to his colourless, crystalline santal, $C_8H_6O_3$, a bright red substance, $C_{14}H_{12}O_4$, soluble in alkaline solutions with a purplish-red colour. Curiously enough, in the more recent accounts of sanderswood, this paper appears to have been lost sight of.

The present investigation, although commenced a considerable

* A less known insoluble red wood is the Narra wood of the Philippine Islands, *Pterocarpus*, spp., which has been investigated by Brooks (*loc. cit.*).

time ago, is of necessity somewhat incomplete, and must remain so for the present, on account of other work which in the present circumstances is of greater importance.

EXPERIMENTAL.

In order to obtain some idea as to the solvent properties of the constituents of camwood, the fractional extraction of a few grams of the powdered wood in a Soxhlet apparatus was first carried out, and for the sake of comparison, samples of barwood and sanders-wood were similarly treated. Employing in the order given, benzene, ether, ethyl acetate, acetone, and alcohol, fractions very similar in appearance were obtained from each of these woods, as if, indeed, all contained the same constituents. From the behaviour of the solvents, however, it became apparent that more than one colouring matter was present, for, after the removal of colourless substances by means of benzene, ether somewhat slowly dissolved a red colouring matter, and when this ceased to pass into solution, a considerable amount of a brownish-red substance, evidently the main product, was extracted by means of commercial ethyl acetate. Subsequently, by means of acetone, a small amount of a similar compound was isolated, whereas the final alcoholic extract contained traces of a darker and somewhat uninviting-looking product.*

In working with camwood on the larger scale, such a process was impracticable, and an alcoholic extract was first prepared. In order to isolate the mixed colouring matters, the precipitation of these as lead salts by means of lead acetate according to Meier's method (*Arch. Pharm.*, 1848, **55**, 285) was at first adopted, but the subsequent filtration processes were so extremely tedious that a more rapid method was devised. This consisted in the addition of concentrated barium hydroxide solution to the wood extract in boiling 80 per cent. alcohol, there being thus formed a precipitate of the barium salt, which filtered rapidly, and was subsequently washed with 80 per cent., and finally with boiling alcohol. The reddish-brown precipitate suspended in water was decomposed by means of dilute hydrochloric acid, the crude colouring matter collected, and, in order to remove as far as possible obstinately retained mineral matter, boiled two or three times with 5 per cent. hydrochloric acid solution. When cold, the product was repeatedly ground with water to decompose completely the oxonium hydrochloride present.

* By exhaustion with alcohol, camwood gave 16 per cent. and sanderswood 19·4 per cent. of extract.

The dried substance was now dissolved in a little alcohol, the solution stirred with purified sand, the alcohol removed by evaporation, the residue finely ground, and extracted in a large Soxhlet apparatus with commercial ethyl acetate. At the end of the operation some quantity of the colouring matter had separated out (*A*), and from this the supernatant liquid was decanted, evaporated to a small bulk, and poured into ether, causing the deposition of some quantity of brown precipitate, which was added to *A*. That fraction soluble in ether is referred to later as *B*.

A was dissolved in absolute alcohol, the solution treated at about 60° with alcoholic potassium acetate solution, and the voluminous precipitate of the potassium salt collected and washed with alcohol (compare Cain and Simonsen, *loc. cit.*). It was decomposed in warm aqueous suspension with dilute sulphuric acid, the reddish-brown product, after washing, allowed to dry on porous porcelain, dissolved in a little alcohol, and reprecipitated by pouring into ether. Finally, it was digested with boiling purified ethyl acetate, which removed a trace of more readily soluble substance, and repeatedly washed with the same solvent.

Found: C=65·68, 65·49; H=5·47, 5·52.

$C_{15}H_{14}O_5$ requires C=65·69; H=5·11 per cent.

This substance, for which the name iso*santalin* is proposed, consists of a dark chocolate-coloured powder which on grinding becomes redder in appearance. As deposited from dilute alcohol, it could not be obtained in a definitely crystalline condition, and although when isolated from ethyl acetate the product frequently exhibited minute serrated edges, detached crystals have as yet not been observed. When heated, it showed no signs of melting, had darkened at 280°, and was fully decomposed at 290—300°, being then a carbonaceous powder. It is readily soluble in boiling methylated spirit, but with hot absolute alcohol, it resinifies and does not readily pass into solution. The general properties of this substance are described later in comparison with those of santalin.

Although the elementary analysis of *iso*santalin was in agreement with the formula $C_{15}H_{14}O_5$ proposed for santalin by Cain and Simonsen, Zeisel determinations* of the former showed that it could not possess this formula, which would require, as determined by these authors, CH_3=5·47 per cent. Indeed, the best expression for the figures obtained is given below, as the result of the analysis of numerous preparations dried at 160°.

* These were carried out by Perkin's method, with and without acetic anhydride, and employing as a precaution bulbs containing a suspension of amorphous phosphorus.

Found: $CH_3=6\cdot82$, $7\cdot01$, $7\cdot03$, $6\cdot85$, $7\cdot30$.

$C_{22}H_{16}O_5(O\cdot CH_3)_2$ requires $C=65\cdot75$; $H=5\cdot02$; $CH_3=6\cdot85$ per cent.

The potassium salt, prepared with boiling alcoholic potassium acetate, was repeatedly washed with alcohol, and consisted of an amorphous, reddish-brown powder. In case the *iso*santalin is impure, the precipitate is not granular at this temperature, but congeals to resinous lumps.

Found: $K=2\cdot71$, $3\cdot03$, $3\cdot08$, $3\cdot06$, $2\cdot26$.

$(C_{24}H_{21}O_8K)(C_{24}H_{22}O_8)_3$ requires $K=2\cdot18$ per cent.

$C_{72}H_{65}O_{24}$ requires $K=2\cdot88$ per cent.

These figures were again distinct from those obtained by others for the potassium salt of santalin, $C_{30}H_{27}O_5K$, which requires $K=6\cdot76$ per cent.

To decide between the two formulæ given above is not easy, for although the latter agrees best with the analyses obtained, *iso*santalin obstinately retains traces of ash which naturally accumulate in the precipitate, and, again, this amorphous potassium salt is not easy to wash. When an alcoholic solution of *iso*santalin is treated with a mineral acid, an intense reddish-violet solution is obtained, which is evidently due to the formation of an oxonium salt. These compounds, owing to their ready solubility in alcohol and acetic acid, could not be satisfactorily isolated, although the hydrobromide, which is fairly stable, can be obtained on evaporating its alcoholic solution as a black, glassy mass. They are also produced to some extent in the insoluble form by the action of hot dilute aqueous acid, and are gradually decomposed in contact with water, with regeneration of the reddish-brown colour of the original dye.

Acetyl Derivative.—The substance was digested with boiling acetic anhydride and a trace of pyridine for three hours, and the solution poured into water. The precipitated product when dry was dissolved in benzene, the solution filtered if necessary, and poured into light petroleum. The deep salmon-coloured powder was finally washed with a little ether.

Found: $C=63\cdot54$; $H=4\cdot95$.

$C_{24}H_{18}O_8(C_2H_3O)_4$ requires $C=63\cdot36$; $H=4\cdot95$ per cent.

An acetyl determination by the ethyl acetate method gave $C_2H_4O_2=39\cdot67$, whereas the above formula requires $C_2H_4O_2=39\cdot60$ per cent. These figures are very similar to those found by Cain and Simonsen for acetylsantalin.

It did not possess a definite melting point, but gradually decomposed without fusion between 250° and 280°, forming a carbon-

aceous powder. It was readily soluble in benzene, sparingly so in alcohol, and has not been obtained as yet in a definitely crystalline condition.

A molecular weight determination, employing naphthalene as solvent, gave the following result:

0·633 in 13·5 naphthalene gave $\Delta t = -0 \cdot 14^\circ$. M.W. = 2344.

This small depression did not appear to arise from a separation of the substance during the crystallisation of the naphthalene. The result is interesting, as it approximates to the formula $[C_{24}H_{18}O_7(C_2H_3O)_4]_4$, M.W. = 2360, which accords with the formation of the potassium salt, $C_{96}H_{87}O_{32}K$, previously referred to. Whereas the substance on the one hand may be regarded as itself highly associated, it is quite probable that the association occurs in the solution of naphthalene or that a colloidal solution is thus produced. Complex salts, again, of the character of potassium *iso*santalin can be obtained from simple substances, such as gallacetophenone (T., 1903, **83**, 131), which with aqueous potassium acetate forms potassium trigallacetophenone, $C_{24}H_{23}O_{12}K$.

Examination of the Fraction B.

Whereas *iso*santalin is almost entirely precipitated when its concentrated alcoholic solution is poured into ether, a second colouring matter is present which in these circumstances remains dissolved. The residue obtained by evaporation of the extract gave C = 66·54, H = 5·61, CH_3 = 8·06 per cent., figures indicating in the light of later results the presence of *iso*santalin and a third substance of high methoxy-content as impurities. With the object of removing the former, a concentrated alcoholic solution was poured into much benzene, the resinous precipitate, which separated in small quantity, removed, and the highly fluorescent liquid gradually evaporated. Any deposit which quickly separated was neglected, the clear liquid concentrated until bright red flocks separated, and these were collected and washed with benzene.

A more rapid method of isolating this substance, although in a cruder form, was to pour a concentrated alcoholic extract of the wood into boiling benzene, and to submit the liquid to fractional evaporation. The product could be obtained purer by a second treatment in the same manner. The bright scarlet powder obtained by these methods gave CH_3 = 8·10 per cent., a figure showing no reasonable connexion with *iso*santalin, and further purification was evidently necessary. This was effected by treating a concentrated solution of the colouring matter in alcohol with

a little hydrobromic acid, and repeatedly shaking the liquid with ether, in which the hydrobromide is insoluble.* The solution of the latter was now poured into water, and in order completely to remove hydrobromic acid, the mixture was gently warmed with sodium acetate solution. Finally, the compound thus isolated was dried on sand, extracted with ether, the liquid diluted with a little benzene, and the red deposit which separated during evaporation washed with benzene.

Found: C=67·63; H=5·33; CH_3=7·13, 7·42.

$C_{24}H_{24}O_7$ requires C=67·92; H=5·65; CH_3=7·08 per cent.

Such a formula, which represents this compound as *iso*santalin less one atom of oxygen, but richer in hydrogen, suggests the replacement of a CO-grouping in the latter by CH_2, but as this for the present must remain hypothetical, the compound will be tentatively referred to as *deoxy*iso*santalin*.

It consists of a scarlet, amorphous powder which has not yet been obtained in a definitely crystalline condition. When heated, the preparation did not show any well-defined melting point, but decomposed at 160—165° with the evolution of gas. It is readily soluble in pure ethyl acetate, sparingly so in ether, and is again distinguished from *iso*santalin by the redder shades it gives on dyeing and the redder tone of its alkaline solutions. A fuller account of these is given later. When a solution of the substance in absolute alcohol is treated with potassium acetate, no immediate precipitation of potassium salt occurs as happens in the case of *iso*santalin, and only when excess of the reagent is employed is a gelatinous deposit formed. The presence of this is no doubt responsible for the resinous condition of impure potassium santalin when this is prepared in the presence of boiling alcohol. It was acetylated by boiling with acetic anhydride and pyridine, and the product, isolated by means of water, was dissolved in benzene, precipitated by light petroleum, and subsequently washed with pure ether.

Found: C=64·34, 64·61; H=5·40, 5·29; $C_2H_4O_2$=39·67, 39·94.

$C_{24}H_{20}O_7(C_2H_3O)_4$ requires C=64·86; H=5·40; $C_2H_4O_2$=40·53 per cent.

*Acetyldeoxy*iso*santalin* thus contains the same number of acetyl groups as acetyl*iso*santalin. It consists, when dry, of an almost colourless powder, differing considerably in appearance from acetyl*iso*santalin, and is also more readily soluble in benzene. When heated, it fused and decomposed at 170—175°:

* The ethereal liquid contained some quantity of an almost colourless phenolic substance which did not appear to be readily susceptible of crystallisation.

0·7485 in 12·13 naphthalene gave $\Delta t = -0{\cdot}325°$. M.W. = 1324.
$(C_{32}H_{32}O_{11})_2$ requires M.W. = 1184.

Acetyldeoxy*iso*santalin in these circumstances thus shows approximately one-half the molecular weight of acetyl*iso*santalin, a property again distinguishing these two substances.

Sanderswood.

Although *iso*santalin closely resembled in its general reactions the santalin of sanderswood, the formula $C_{15}H_8O_3(O{\cdot}CH_3)_2$ assigned to the latter by earlier workers nevertheless pointed to a considerable difference between the two substancs. For purposes of comparison, an alcoholic solution of sanderswood was prepared, the colouring matter isolated by means both of lead acetate and baryta, and the product worked up by identical methods to those previously employed with camwood. As a result, it was found that the phenolic constituents of both woods closely resembled one another in general properties, and two distinct compounds, santalin and deoxysantalin, corresponding with *iso-* and deoxy*iso*-santalin, were isolated. The santalin was finally purified by extraction with purified ethyl acetate, and could be subsequently crystallised from dilute alcohol.

Found: C = 65·70; H = 4·90; CH_3 = 6·81, 7·09.
$C_{15}H_{14}O_5$ requires C = 65·7; H = 5·11; CH_3 = 5·47 per cent.
$C_{24}H_{22}O_8$,, C = 65·8; H = 5·02; CH_3 = 6·85 per cent.

Santalin is therefore isomeric with *iso*santalin, and cannot possess the formula $C_{15}H_{14}O_5$. It consisted of a chocolate-coloured powder, very similar in appearance to *iso*santalin, readily soluble in hot methylated spirit, although with absolute alcohol it resinified and dissolved with difficulty. When heated, it commenced to soften at 243°, decomposed at 250—260°, and at 270° had become a honeycombed, carbonaceous mass. Cain and Simonsen (*loc. cit.*) describe santalin as melting at 223—226°, but from the examination of the colouring matter isolated according to their direction and in other ways, it seemed certain that santalin decomposes at about the temperature stated above, and does not possess a distinct melting point. The decomposition of this substance, however, occurs at a much lower temperature than in the case of *iso*santalin. It was first pointed out by one of us (T., 1899, **75**, 443) that the commercial santalin of Merck yielded with alcoholic potassium acetate a maroon-coloured salt, which on analysis gave K = 6·94, corresponding with the formula $C_{30}H_{27}O_{10}K$. Although in this case, as was indeed indicated, the reaction was

only given as a general illustration of the potassium acetate method, this result appeared to be correct, for not only was it confirmed by Cain and Simonsen, but Brooks again (*Philippine J. Sci.*, 1910, 5, 448) obtained from narrin an allied colouring matter of narra wood, *Pterocarpus*, spp., a copper salt, $(C_{15}H_{13}O_5)_2Cu$. Experiments now carried out with pure santalin gave a very different result, the potassium salt prepared by means of boiling potassium acetate giving K=2·45 per cent., a figure very similar to that yielded by potassium *iso*santalin.

There was some reason to suspect that the commercial santalin sample just referred to represented the precipitate derived by acidification of an alkaline extract of the wood, and as it is known that in this way some alteration of the colouring matter, or at least a portion of it, occurs, it was interesting to examine the potassium salt obtained from this crude material. Such a preparation, although very thoroughly washed, contained free mineral matter, and the potassium salt derived from it gave K=4·01 per cent. This result, although higher than that given by pure santalin, is not sufficiently so to explain the analysis of the original product, which would thus appear to have contained much free mineral matter.

The potassium salt of santalin may thus be represented, as in the case of the *iso*santalin compound, as either $C_{72}H_{65}O_{24}K$ or $C_{96}H_{87}O_{32}K$.

Santalin in alcoholic solution shows evidence of the formation of soluble oxonium salts with mineral acids, and although it closely resembles *iso*santalin, gives colour reactions which indicate that it is not the same substance.

	Santalin.	iso*Santalin.*
Alcoholic hydrobromic acid	Crimson	Reddish-violet
Dilute sodium hydroxide	Dull red	Dull violet
Alcoholic ferric chloride.................	Violet	Bluish-violet

Again, the solution of *iso*santalin in alcohol is much browner than that of santalin. Somewhat more marked are the differences in shade given by these colouring matters in similar circumstances, especially when mordants are employed. For dyeing the colouring matter, 0·25 gram in alcoholic solution was added to the water in the dye-bath, and the dyeings were carried out (*a*) employing wool alone, (*b*) employing wool alone and subsequently saddening with bichrome, (*c*) employing wool mordanted with bichrome and cream of tartar, and (*d*) employing wool mordanted with bichrome and sulphuric acid. The results obtained were as follows:

	(a)	(b)	(c)	(d)
Santalin ...	Pale dull red	Dull reddish-brown	Pale reddish-pink	Pale reddish-pink
*iso*Santalin	Pale violet-red	Dull violet-maroon	Violet-red	Violet-red, weaker than (c).

Acetylsantalin, prepared in the same way as acetyl*iso*santalin, closely resembled the latter in appearance.

Found: $C_2H_4O_2 = 39{\cdot}58$, $38{\cdot}96$.

$C_{24}H_{18}O_8(C_2H_3O)_4$ requires $C_2H_4O_2 = 39{\cdot}6$ per cent.

It consisted of a deep salmon-coloured powder, which commenced to decompose at about 225°, and at 255—260° swelled up to form a carbonaceous mass:

0·7258 in 12·03 naphthalene gave $\Delta t = -0{\cdot}165°$. M.W. = 2558.

The small depression thus obtained is similar to that given by acetyl*iso*santalin, and approximates to the formula $(C_{32}H_{30}O_{12})_4$.

Deoxysantalin.

Sanderswood resembles camwood in containing a second, more readily soluble colouring matter, for which the name *deoxysantalin* is suggested. It may be prepared according to the method given for the isolation of deoxy*iso*santalin.

Found: $C = 67{\cdot}59$, $68{\cdot}10$; $H = 5{\cdot}08$, $5{\cdot}70$; $CH_3 = 7{\cdot}21$.

$C_{24}H_{24}O_7$ requires $C = 67{\cdot}92$; $H = 5{\cdot}65$; $CH_3 = 7{\cdot}08$ per cent.

It consists of a bright red powder, the ethereal solution of which possesses a greenish fluorescence, but it has not yet been obtained in a crystalline condition. Alcoholic potassium acetate gives no immediate precipitate of potassium salt, but after some time or by means of excess of the reagent a gelatinous deposit separates. A comparison of the colour reaction of deoxysantalin (*a*) and deoxy*iso*santalin (*b*) are given in the following table. These, compared respectively with santalin and *iso*santalin (see earlier), possess much yellower tones.

	(a)	(b)
Alcoholic solution	Orange-brown	Orange
Alcoholic hydrobromic acid	Scarlet	Bright crimson
Dilute sodium hydroxide	Scarlet	Crimson-scarlet
Alcoholic ferric chloride....................	Maroon	Violet

The dyeing experiments were carried out by the processes which were adopted with santalin and *iso*santalin.

	(a)	(b)	(c)	(d)
Deoxysantalin...	Red	Dull bluish-red	Dull crimson	Red
Deoxy*iso*santalin	Pale reddish-violet	Red-puce	Dull reddish-violet	Pale dull reddish-violet

As a result, it was found that although in general character the shades given by santalin and deoxysantalin are similar, the latter is by far the better dye, possessing a stronger and brighter appearance. The difference between *iso*santalin and deoxy*iso*santalin in this respect was not so marked, and, if anything, was in favour of the former.

Acetyldeoxysantalin was obtained as an almost colourless amorphous powder, readily soluble in benzene.

Found: $C=64{\cdot}43$; $H=5{\cdot}50$; $C_2H_4O_2=39{\cdot}30$.
$C_{24}H_{20}O_7(C_2H_3O)_4$ requires $C=64{\cdot}86$; $H=4{\cdot}50$; $C_2H_4O_2=40{\cdot}52$ per cent.

Deoxysantalin is thus isomeric with deoxy*iso*santalin.

The first isolation of a colouring matter from sanderswood was carried out by Meier (*loc. cit.*), who employed ether as a solvent, and describes this as red, microscopic prisms melting at 104—105°, but did not analyse his product. A repetition of Meier's process failed to give the substance in a crystalline condition, as, indeed, Weyermann and Haffely (*loc. cit.*) found, but the product was interesting in that it evidently consisted mainly of deoxysantalin, being bright red and giving no immediate precipitate with alcoholic potassium acetate. This was not to be wondered at, as pure santalin is not soluble in pure ether.

In the hope of obtaining the colouring matter in a crystalline form, wool was dyed with sanderswood in the usual manner, and attempts were made to extract it by means of solvents from the fibre, but without success. Although the exact reason for its insolubility was not determined, it seems likely that it is there fixed as an acid calcium salt, because only by steeping the dyed material in 33 per cent. hydrochloric acid overnight did it then dissolve in the usual way. The material, subsequently well washed and dried, was extracted with ether, and the fluorescent extract was evaporated to dryness and the residue washed first with benzene and then with water to remove acid. It was again extracted with ether, benzene added to the extract, and the red flocks which separated on evaporation were washed with benzene. The small amount of bright red powder thus isolated had the properties of deoxysantalin, and has hitherto failed to yield crystals. A methoxy-determination gave $CH_3=6{\cdot}58$ per cent. It thus seems that the dyeing property of sanderswood is due rather to the deoxysantalin than to santalin itself, and again, although sanderswood is specially rich in colouring matter, it is astonishing how little of this comes into play in the dyeing process.

Some proof of this was obtained by dyeing wool with 60 per cent.

of sanderswood, and at the end of the operation employing the residual wood twice for dyeing fresh material. The first pattern possessed the usual colour, the second was pale pink, and the third was practically undyed, indicating that all the colouring matter soluble in water had then been removed. The woody matter, however, now yielded to boiling alcohol 13·8 per cent. of extract compared with the 19·4 per cent. originally present, and this consisted of a dark red, resinous mass and contained much santalin. Even, therefore, if it be presumed that all the soluble matter removed from the wood in the dye-bath is colouring matter, it is evident that the larger proportion present therein, owing to its insoluble nature, remains undissolved and takes no part in this operation.

Weidel (*loc. cit.*), by removing the colouring matter from sanderswood with dilute alkali hydroxide, precipitating with acid, and extracting the product with ether, isolated two crystalline compounds, namely, santal, $C_8H_6O_3$, and a red substance, $C_{14}H_{12}O_4$, very sparingly soluble in the ordinary solvents. Experiments to isolate these compounds by Weidel's process have hitherto failed, although, as shown later, they can be obtained from barwood. As in any case they are difficult to prepare, especially by his method, a definite statement as to their non-existence in sanderswood cannot at present safely be made.

On the other hand, sanderswood contains, like camwood, a colourless, phenolic substance not removed from ether by means of hydrobromic acid, which does not appear to crystallise readily.

Barwood.

A comparison of the colouring matter of this wood with those of sanderswood and camwood appeared to be interesting, but owing to lack of opportunity its examination in this respect could not be carried out at all completely, and the extract from only 450 grams of the wood has as yet been employed.

The only important work on this subject is that of Anderson (*Journ. Chem. Soc.*, 1876, ii, 582), which, curiously enough, has been ignored in the later literature. He obtained from the wood colourless crystals, which he termed baphiin, and from this product by means of alkali solution prepared baphic acid, soluble in this reagent, and baphinitin and baphinitone, insoluble, all of which were also crystalline. According to Ryan and Fitzgerald (*Proc. Royal Irish Acad.*, 1913, **30**, 106), baphinitone is identical with homopterocarpin, and possesses the formula $C_{17}H_{16}O_4$. Anderson also considered the wood to contain three colouring matters, one

soluble in ether, a second soluble in alcohol and insoluble in ether, and a third which is crystalline.

The alcoholic extract* of barwood was worked up in the same manner as that of camwood and sanderswood, and a colouring matter corresponding with the santalin and *iso*santalin of the latter was isolated. After treatment with pure ethyl acetate, it consisted of a chocolate-red powder indistinguishable in appearance from santalin. The analysis of this substance and of its potassium salt gave the following result:

Found: C = 65·8; H = 4·6; CH_3 = 7·43; K = 3·06.

On heating, it commenced to soften at 240°, apparently decomposing, and at 270° had the appearance of a honeycombed, carbonaceous mass, a behaviour very similar to that given by santalin; its colour reactions, which were violet with alcoholic ferric chloride, crimson with alcoholic hydrobromic acid, and dull red with dilute sodium hydroxide solution, were the same as those given by this colouring matter. It thus appears extremely probable that this is identical with santalin.

The ethereal liquid obtained during the isolation of this substance, which corresponded with that termed *B* in connexion with camwood, was evaporated to dryness, the residue again dissolved in a little alcohol, and poured into ether. The solution decanted from a trace of resinous precipitate was washed once with water and treated drop by drop with fuming hydrobromic acid until all the colouring matter had been removed from the ether as hydrobromide (*C*). After washing with water, the ether, on evaporation to dryness, gave an almost colourless, crystalline residue. This was digested with benzene to remove a trace of a substance resembling pterocarpin,† dissolved in hot alcohol, and the solution diluted with a little water. The large leaflets which separated on cooling and became opaque on drying, owing to loss of water of crystallisation, were recrystallised from absolute alcohol. The yield was 0·7 gram.

Found: C = 63·95; H = 4·20; CH_3 = 5·04.

$C_{16}H_{12}O_6$ requires C = 64·0; H = 4·0; CH_3 = 5·0 per cent.

This compound appears to be the santal described by Weidel (*loc. cit.*) as existing in sanderswood; he assigned to it the formula $C_8H_6O_3,\frac{1}{2}H_2O$, and obtained from it a dibromo-compound,

* The residue obtained by evaporating the alcoholic extract to dryness on solution in 75 per cent. alcohol gives gradually a considerable deposit of this product.

† The complete removal of this substance from the colouring matter by either the lead acetate or baryta method of precipitation is difficult to effect.

$C_8H_4O_3Br_2$. Weidel, however, did not ascertain the presence of a methoxy-group, and its analysis in this respect indicates that it possesses the formula $C_{15}H_9O_5(O{\cdot}CH_3)$. Santal melts at 222—223°, is readily soluble in dilute alkali hydroxide, and sparingly so in absolute alcohol, from which it crystallises in thin plates or flat needles. With alcoholic lead acetate, it gives a colourless precipitate, and with alcoholic ferric chloride a violet-black coloration, although this, according to Weidel, is dark red. On acetylation, it gives a well-defined, crystalline acetyl derivative, and seems to be very similar to Anderson's baphic acid (*loc. cit.*). The hydriodic acid liquid from the Zeisel determination contained crystals, and these, after removal of the acid, separated from dilute alcohol in small, colourless, flat needles melting at 270—273°, apparently with decomposition. This new compound, for which the name *santol* is proposed, would appear to possess the formula $C_{15}H_{10}O_6$, and this it is hoped to confirm at a later period. Its solution in dilute alkali hydroxide, at first almost colourless, rapidly develops a reddish-violet tint, and the liquid on acidification deposits yellow crystals. If the acid mixture is boiled, these become colourless, apparently with regeneration of santol, for when collected and washed, the product can again be made to produce the same changes. Santol thus appears to contain a lactone group. With lead acetate, it gives a colourless precipitate, and with alcoholic ferric chloride a brownish-black coloration.

The hydrobromic acid liquid (*C*) obtained during the isolation of santal, decanted from any insoluble matter, was diluted with water, the precipitate repeatedly treated with water to decompose the hydrobromide, and the product, when dry, dissolved in a little ethyl acetate, the solution being allowed to evaporate spontaneously. After several days, minute specks were present in the viscous fluid, and this was now stirred with a mixture of pure ether and ethyl acetate, the insoluble product being collected and washed with ethyl acetate In order to remove santal, which was found to be present, it was digested at the boiling point for one hour with absolute alcohol, and the glistening mass of bright red crystals (0·4 gram) analysed. (Found: $C=67{\cdot}3$; $H=4{\cdot}8$; $CH_3=9{\cdot}77$.)

This had the reactions of the compound $C_{14}H_{12}O_4$ ($C=68{\cdot}8$; $H=4{\cdot}9$) described by Weidel as existing in sanderswood, but probably contained still a little santal, and this seemed certain by a crystallisation of the substance from alcohol, when the 0·0756 gram thus obtained gave the higher figures, $C=67{\cdot}86$; $H=4{\cdot}84$ per cent. A further purification has not been possible, but there can be little doubt that this compound still retained santal, and that when completely freed from this, Weidel's formula, $C_{14}H_{12}O_4$, represents its

composition. On the other hand, the result of the Zeisel determination indicates that Weidel's formula can scarcely be correct, and that the true formula, based on his figures, would appear to be $C_{22}H_{13}O_4(O\cdot CH_3)_3$ or $C_{22}H_{15}O_4(O\cdot CH_3)_3$, the former of which requires $C = 69{\cdot}1$; $H = 5{\cdot}06$; $CH_3 = 10{\cdot}3$ per cent. In case this is correct, this compound, for which the name *santalone* is proposed, has the composition of *deoxysantalin monomethyl ether*, and, indeed, its general properties are in harmony with this suggestion.

Santalone is sparingly soluble in most solvents, and crystallises from alcohol in small, glistening red leaflets. It readily dissolves in alcoholic hydrobromic acid with a bright scarlet, in dilute alkalis with a fairly permanent red, whereas alcoholic ferric chloride produces a violet colour. Alcoholic potassium acetate does not appear to cause the separation of a potassium salt. When heated, the purest preparation obtained up to the present darkened about 280° and melted at 300°.

The hydriodic acid liquid from the Zeisel determination contained a blackish-green, metallic-looking resin, which was soluble in alkali hydroxide with a violet colour, rapidly becoming brown in the air and closely resembling the product given in the same way by deoxysantalin.

Several years ago Herz and Perkin (Thorpe's "Dictionary of Applied Chemistry," 1913, Vol. IV., 629) isolated both these compounds from barwood by Weidel's method in very small amount, but in order to obtain any quantity of this rare material, the process of extracting large quantities of resinous colouring matter with ether for several days proved impracticable. On the other hand, the operation was not always successful, and this appeared to depend on the alteration of the main bulk of the constituents of the wood soluble in ether, other than santal and santalone, during the alkaline extraction into resinous products insoluble in this medium.

The mother liquors from which the santalone had been isolated contained a considerable amount of insoluble colouring matter resembling deoxysantalin, which, however, was not closely examined.

Summary of Results.

The results of this investigation indicate that the more insoluble colouring matter of camwood, here termed iso*santalin*, is most simply expressed as $C_{22}H_{18}O_6(OMe)_2$. It is isomeric with the santalin of sanderswood, and for this the same formula is therefore proposed in place of $C_{14}H_{11}O_4(OMe)$ suggested by Cain and

Simonsen. Although santalin from sanderswood appears to be identical with the colouring matter which can be similarly isolated from barwood, the *iso*santalin of camwood differs from both these in that it possesses not only a much higher decomposition point, but gives distinctly bluer shades on mordanted woollen cloth. *iso*Santalin and santalin are respectively accompanied in the dye-wood by the more readily soluble colouring matters *deoxy*iso*santalin* and *deoxysantalin*, which again are isomeric, and for which the formula $C_{22}H_{16}O_5(OMe)_2$ or $C_{22}H_{18}O_5(OMe)_2$ is proposed. The connexion between the santalins and deoxysantalins is at present uncertain, and the acetyl determinations do not favour the view which at first suggested itself, that the former differ from the latter in possessing an additional hydroxyl group. There is some probability that the deoxy-compounds are converted by oxidation in alkaline solution into the santalins, but experiments on this point and on their behaviour towards *p*-benzoquinone in alcoholic solution have for the present been laid aside. None of these compounds has as yet been obtained in a definitely crystalline condition, and the opinion is expressed, at least as regards santalin, that if this is to be effected some special process, perhaps of the character by which crystalline hæmatein is prepared from logwood, will have to be devised. Meier's santalin (*loc. cit.*), which it is suggested is rather deoxysantalin than Cain and Simonsen's santalin, was described by this author as crystalline, and it is quite possible that both deoxy- and deoxy*iso*-santalin, here obtained, contain still some impurity which renders crystallisation more difficult. The potassium salts of *iso*santalin and santalin possess the formula $C_{72}H_{65}O_{24}K$ or $C_{96}H_{87}O_{32}K$, and this fact, coupled with the exceedingly small depression of the freezing point given by their acetyl compounds in naphthalene, indicates that either these colouring matters possess a very high molecular weight or that this depression is abnormal. The effect of other solvents remains to be investigated, but as Cain and Simonsen, employing phenol, obtained with santalin a molecular weight of 257, the latter suggestion would appear to be correct.

Santal and Weidel's substance, $C_{14}H_{12}O_4$ (?), now termed *santalone*, have been found to exist in barwood, and the formulæ considered applicable to these compounds are respectively $C_{15}H_9O_5(OMe)$ and $C_{22}H_{15}O_4(OMe)_3$, the latter being possibly a *deoxysantalin monomethyl ether*. These compounds will be further examined when opportunity arises, and it is possible that by their study some clue to the constitution of both santalin and *iso*santalin will result.

Note on St. John's Wort.

According to Keegan (*Chem. News*, 1915, **111**, 290), St. John's wort, *Hypericum perforatum*, contains much flavone, which seemed to be similar to gossypetin. Desiring a further supply of this colouring matter, previously only known to be present in quantity in cotton flowers, the yellow colouring matter of St. John's wort was submitted to examination. A concentrated alcoholic extract of the dried material was poured into water, the mixture shaken with ether to remove wax, etc., and the clear liquid digested at the boiling point with a little sulphuric acid. When cold, the precipitate was collected, and in this condition dissolved in alkali with a green shade somewhat similar to that given by gossypetin. After removal of impurity by solution in ether, the yellow product was crystallised from dilute alcohol, and on treatment with alkali hydroxide now gave a pure yellow tint. The acetyl compound melted at 194—196°, and when mixed with acetyl quercetin did not depress the melting point of the latter. The benzoyl compound melted at 185—186°, and this was identical with that of pentabenzoyl quercetin obtained by means of benzoic anhydride. The colouring matter of St. John's wort consists, therefore, of quercetin, and no gossypetin is present.

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XVII.—*Studies on the Walden Inversion. Part VI. The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylbromoacetic Acid to Phenylaminoacetic Acid.*

By GEORGE SENTER and STANLEY HORWOOD TUCKER.

IN previous papers (Senter and Drew, T., 1915, **107**, 638; 1916, **109**, 1091) it was shown that when the halogen atom in optically active phenylchloroacetic acid is displaced by the amino-group by the direct action of ammonia, the sign of the amino-acid depends on the nature of the solvent in which the reaction occurs. In water, the higher aliphatic alcohols, and benzonitrile, the resulting amino-acid has the opposite sign to the chloro-acid taken, whereas

in liquid ammonia, acetonitrile, and the lower aliphatic alcohols, the amino-acid has the same sign as the original chloro-acid. In all cases, the amino-acids obtained were considerably less active than the optically pure acids, so that considerable racemisation occurred during the displacement. In order to throw further light on this question, a similar investigation has now been carried out with phenylbromoacetic acid, and the results are described in the present paper. In addition to the amino-acid, iminodiphenyldiacetic acid is also formed in all the solvents used. The reactions are as follows:

$$Br{\cdot}CHPh{\cdot}CO_2{\cdot}NH_4 + NH_3 \longrightarrow NH_2{\cdot}CHPh{\cdot}CO_2H + NH_4Br,$$

$$2Br{\cdot}CHPh{\cdot}CO_2{\cdot}NH_4 + NH_3 \longrightarrow CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}CO_2H + 2NH_4Br.$$

The method of experiment was similar to that used in the case of the chloro-acid (*loc. cit.*). In all cases, *l*-phenylbromoacetic acid was used, and the reactions took place at the ordinary temperature. As the amino-acid and imino-acid from most of the solvents were opposite in sign, special care was taken to ensure the purity of the products before their optical activity was determined. The rotatory power of the products was measured with mercury green light ($\lambda = 5461$), in most cases also with sodium light, and in some cases with the mercury violet ($\lambda = 4359$). In numerous measurements with amino-acids of different degrees of activity, it has been found that the ratio $[\alpha]_D : [\alpha]_{5461}$ is 0·84. The observations, both with the amino-acid and imino-acid, were made in *N*-hydrochloric acid solution.

The main results are given in the accompanying table.

TABLE I.

Action of Ammonia on l-*Phenylbromoacetic Acid.*

Solvent.	Value of $[\alpha]_{5461}$ for amino-acid formed.	Value of $[\alpha]_{5461}$ for imino-acid formed.
Liquid NH_3	− 38°	+ 161°
Water	+ 89	+ 177
$CH_3{\cdot}OH$	+ 2	+ 180
$C_2H_5{\cdot}OH$	+ 2	+ 120·5
$C_3H_7{\cdot}OH$ (*n*)	+ 5·5	+ 187·5
$C_3H_7{\cdot}OH$ (*iso*)	+ 3·2	+ 173·5
$C_4H_9{\cdot}OH$ (*n*)	+ 17·7	+ 206
$(CH_3)_3C{\cdot}OH$	+ 22	+ 193
$C_7H_{15}{\cdot}OH$ (*n*)	+ 130	+ 170
$CH_3{\cdot}CN$	− 48·3	[+ 66·7]

The value of $[\alpha]_D^{20}$ for optically pure phenylaminoacetic acid is $\pm 157{\cdot}8°$ (Fischer and Weichhold, *Ber.*, 1908, **41**, 1285), corresponding with $[\alpha]_{5461}^{20}$ $\pm 187{\cdot}8°$.

The amino-acid from each experiment was separated in two crops (p. 146), which were examined separately as regards activity. The second much smaller crop was in almost all cases the more active, corresponding with the fact that the active acids are considerably more readily soluble in water than the racemic. The numbers in the second column represent the mean activity of the whole crop of amino-acid in each case, and as the latter could be isolated fairly completely from the products of reaction, they also represent with considerable accuracy the relative activities of the acids formed in the different solvents. The yields of imino-acid were in all cases smaller than those of the amino-acid, but relatively greater than those obtained in the corresponding experiments with the chloro-acid.

The table shows that in all the solvents except water and acetonitrile, the sign of the amino-acid formed is opposite to that of the amino-acid taken. Further, considerable racemisation occurs in all the solvents used, more particularly in the lower alcohols. The imino-acid formed has in every case the opposite sign to that of the original bromo-acid.

As interesting results were obtained as to the effect of ammonium chloride on the reaction with phenylchloroacetic acid, the effect of ammonium bromide on the reaction now under consideration was examined. In aqueous ammonia, the amino-acid from the solution containing no ammonium bromide gave $[\alpha]_{5461}$ $+131°$, whilst in an exactly corresponding experiment, except that the mixture contained 2 grams of ammonium bromide in 10 c.c., the value $[\alpha]_{5461}$ $+122°$ was obtained for the amino-acid. This slight difference is readily accounted for by the greater amount of washing necessary in the latter case to free the amino-acid from ammonium bromide. In exactly comparable experiments in liquid ammonia, the amino-acid from the solution containing no ammonium bromide gave $[\alpha]_{5461}$ $-38°$; that from the solution containing the salt was quite inactive. As ammonium bromide is one of the products of reaction, it doubtless causes some racemisation in certain solvents to which it is not originally added. In the higher alcohols and acetonitrile, it separates in the solid form as the reaction proceeds, and therefore cannot appreciably influence the activity of the amino-acid formed.

Discussion of Results.

Although in many respects the results obtained with phenylbromoacetic acid correspond with those found for the chloro-acid (*loc. cit.*), there are also important differences which will undoubtedly prove of great importance in elucidating the mechanism of the reactions. The chief resemblances are that in both cases the amino-acids obtained from water and the higher alcohols as solvents are opposite in sign; those from liquid ammonia and acetonitrile similar in sign to the original phenylhalogen acid. Further, the effect of ammonium chloride and bromide respectively on the reactions in aqueous and in liquid ammonia is similar in the two cases. The main difference is that with the lower aliphatic alcohols the amino-acid from phenylbromoacetic acid is opposite in sign, from phenylchloroacetic acid similar in sign, to the original phenylhalogen acid. The quantitative results are shown in the accompanying table.

TABLE II.

Solvent (alcohol)	Methyl.	Ethyl.	Propyl.	*iso*Propyl.
Amino-acid from *l*-bromo-acid	+ 2°	+ 2°	+ 5·5°	+ 3·2°
Amino-acid from *d*-chloro-acid	+ 7·5	+ 34	+ 10	+ 5

In a further experiment with *l*-phenylchloroacetic acid in ethyl alcohol, the average activity of the resulting amino-acid was $[\alpha]_{5461}$ $-51°$, which fully confirms the earlier results of Senter and Drew (*loc cit.*). The slightly higher activity in the former case is doubtless due to the lower temperature at which the reaction took place. It may be added that not much confidence from a quantitative point of view can be placed in the results with phenylchloroacetic acid in methyl alcohol, as owing to the simultaneous formation of phenylmethoxyacetic acid only 0·1 gram of phenylaminoacetic acid was obtained, and its activity was doubtless considerably reduced during washing with water. With the other alcohols, good yields of amino-acid were obtained.

The results are probably to be accounted for on the basis of the theory put forward in the succeeding paper (Senter, Drew, and Martin, *loc. cit.*, p. 151), that the action of ammonia on halogen-substituted acids proceeds by two simultaneous reactions, resulting in the formation of *d*- and *l*-amino-acids respectively, and that the relative proportion of the amino-acids formed depends on the nature of the halogeno-acid, of the solvent, and of other factors. In the lower alcohols, the reaction leading to the formation of an amino-acid of the same sign as that of the halogeno-acid predominates

slightly in the case of the chloro-acid, whilst the other reaction predominates slightly in the case of the bromo-acid. In liquid ammonia, the relative rates of the two reactions are influenced considerably by the presence of ammonium bromide. So far, it is not possible to state with certainty which of these reactions is normal and which abnormal, but it is hoped that kinetic investigations will throw light on these and other points.

From the data in table I, it is evident that the amino-acid from the lower alcohols is much more racemised than that from the higher alcohols. This effect, however, is not determined solely by the molecular weight of the alcohol, as the products from isomeric alcohols (the two propyl alcohols, also *n*-butyl alcohol and trimethylcarbinol) are not of the same activity.

Iminodiphenyldiacetic Acid.—The isolation of this acid from the products of reaction is described in the experimental part, and it is there shown that the activity of the optically pure acid probably does not much exceed ±210°. As the table shows, the products from all the solvents are very active; with the doubtful exception of the acid from acetonitrile, $[\alpha]_{5461}$ exceeds 120°. The imino-acids obtained by the action of ammonia on the *d*-chloro-acid (Senter and Drew, *loc. cit.*) were also very active; in aqueous ammonia and ammonium chloride, *n*-butyl alcohol and *n*-heptyl alcohol, the respective values for $[\alpha]_{5461}$ were 188°, 167°, and 162° approximately.

It is shown in the succeeding paper that a corresponding imino-acid, namely, α-imino-$\beta\beta$-diphenyldipropionic acid, is obtained by the action of ammonia on α-bromo-β-phenylpropionic acid in all the solvents examined; in this case, however, the imino-acid has the same sign as the original bromo-acid.

It has already been pointed out (Senter and Drew, *loc. cit.*, p. 1097) that imino-acids of this type might be formed by the reaction of one molecule of ammonia with two molecules of halogeno-acid (p. 141), or by the interaction of one molecule of halogeno-acid and one molecule of amino-acid:

$$Br{\cdot}CHPh{\cdot}CO_2H + NH_2{\cdot}CHPh{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}CO_2H.$$

On the former assumption, the fact that a highly active imino-acid of the same sign is obtained from the same halogeno-acid in all solvents is readily accounted for. The latter view of the mechanism of the reaction would apparently imply that the *l*-bromo-acid reacts with one of the optically active forms of the amino-acid much more rapidly than the other. Thus, it can be calculated from the data in table I that the amino-acid from heptyl alcohol contains

about 85 per cent. of the *d*- and 15 per cent. of the *l*-form, that from liquid ammonia 40 per cent. of the *d*- and 60 per cent. of the *l*-form, whereas from both solvents *d*-imino-acids of high and practically equal activity are obtained. It is well known that an optically active compound may react with one stereoisomeride more rapidly than with the other (compare Marckwald and Meth, *Ber.*, 1905, **38**, 801; Marckwald and McKenzie, *Ber.*, 1899, **32**, 2130), but the differences are usually small, and the predominance of one reaction, which the explanation now under consideration would imply, is so great as to be highly improbable. This question cannot easily be examined experimentally on account of the difficulty of finding a suitable solvent for the amino-acid, but the following observation lends some support to the view that the amino-acid is not an intermediate compound in the formation of the imino-acid. *r*-Phenylaminoacetic acid and *l*-phenylchloroacetic acid, along with triethylamine (which dissolves the former acid only to a small extent), were kept at the ordinary temperature for one hundred and five days. No imino-acid could be isolated from the products, and apparently no reaction had taken place. The conclusion that the imino-acid is formed by the interaction of two molecules of bromo-acid and ammonia therefore appears most in harmony with the experimental results.

It remains to account for the fact that whereas *l*-phenylbromoacetic acid yields a *d*-imino-acid, *l*-benzylbromoacetic acid yields an *l*-imino-acid. As the two *l*-bromo-acids are probably of the same configuration, this result implies either that the two *l*-imino-acids differ in configuration or that a Walden inversion occurs in the formation of one of the imino-acids. Although the latter explanation is the more probable, the former cannot be ruled out, since both for amino-acids and imino-acids the magnitude and even the sign of the rotation are doubtless complicated by internal salt-formation, hydration, and other factors. The effect of change of temperature and addition of electrolytes on the optical activity of the two imino-acids would throw light on the question of their relative configuration (compare Clough, T., 1915, **107**, 1517).

EXPERIMENTAL.

r-Phenylbromoacetic acid was resolved with morphine according to McKenzie and Walker's method (T., 1915, **107**, 1685). The pure *l*-acid melted at 87—88° and gave $[\alpha]^{20}_{5461}$ $-178\cdot5°$, in excellent agreement with the results of these authors. The method of experiment was similar to that used in the case of the chloro-acid, except that the time of reaction was considerably shorter, in accord-

ance with the greater reactivity of the bromo-acid (Senter and Tucker, T., 1916, **109**, 690).

The method of isolating the products already given (Senter and Drew, *loc. cit.*, p. 1098) requires amplification in view of the fact that the separation of the imino-acid was not described. The earlier account is applicable up to the stage at which the first crop of amino-acid has been isolated, and the acidified solution, containing any remaining amino-acid and the other products of reaction, has been extracted several times with ether to remove any unchanged bromo-acid and any non-basic acids (hydroxy-acid, alkyloxy-acid) formed during the reaction. To the aqueous acid solution, which contains the imino-acid and any remaining amino-acid as hydrochlorides, the washings of the first crop of amino-acid are added, the whole is evaporated to dryness to remove excess of hydrochloric acid, the residue dissolved in aqueous ammonia, and the solution evaporated to the stage at which the stirred mass becomes pasty and remains faintly alkaline. In this way, by decomposition of its ammonium salt, the amino-acid is separated in the solid form, and the soluble ammonium salt of the imino-acid remains undecomposed. To the alkaline product cold water is added and the mixture filtered; the residue, after washing with cold water, constitutes the second crop of amino-acid. To the filtrate hydrochloric acid is added until the solution is acid to Congo-red; on keeping, the imino-acid separates in clusters of long needles. If the solution is kept faintly acid, the imino-acid can be separated practically completely; the final solution has a slight activity of the same sign as the amino-acid, due to a trace of the latter which is present on account of its sparing solubility in water.

As already indicated, the method of separating the amino-acid and imino-acid depends on the fact that the unstable ammonium salt of the former is decomposed on heating in solution, the amino-acid separating, whilst the ammonium salt of the imino-acid is stable when heated, even in neutral solution, but decomposes when heated in the dry state at 100°. That the separation was effective was proved in various ways, most convincingly by an experiment in which some imino-acid was added to 0·2 gram of the *r*-amino-acid and the separation carried out in the usual way. The amino-acid obtained proved to be quite inactive, whilst the imino-acid showed its full activity.

The purity of the amino-acid was checked in all cases by a determination of its equivalent by conversion of a known weight into the hydrochloride, and also in some cases by determination of the nitrogen by the absolute method. As in all cases results practic-

ally identical with the calculated values were obtained, it appears unnecessary to quote them in detail.

The activity both of the amino- and imino-acids was measured in 0·984N-hydrochloric acid in a 2-dcm. tube at the ordinary temperature. For the first crops of amino-acid, the solutions contained 1 gram in 100 c.c. of solution ($c=1·0$), whilst usually the whole of the small second crop was used in making up 10 c.c. of solution for activity measurements.

In order to obtain approximately pure *d*-imino-acid, the products from several experiments were recrystallised from N-hydrochloric acid. In one experiment, the third recrystallisation raised the rotation from $[\alpha]_{5461}$ 196° to 200°; in a second experiment, the final crop gave $[\alpha]_{5461}$ +209°. The process could not be carried further owing to want of material, but it is probable that the value of $[\alpha]_{5461}$ for the optically pure acid does not much exceed 210°.

Water.

A solution of 0·5 gram of the *l*-bromo-acid in 10 c.c. of aqueous ammonia (35 per cent. NH_3) was kept at 18° for eight days. The first crop of amino-acid (0·16 gram) had α_{5461} +1·78°, $[\alpha]_{5461}$ +89°; the second crop was so small that the activity could not be measured. The imino-acid (0·015 gram), $c = 0·113$, had α_{5461} +0·40, $[\alpha]_{5461}$ +177°.

In two parallel experiments to determine the effect of ammonium bromide on the reaction, solutions of 0·5 gram of the *l*-bromo-acid in 10 c.c. of aqueous ammonia (35 per cent. NH_3), and in one case 2 grams of ammonium bromide, were kept for nine days at 10°. The solutions remained clear throughout. From the solution containing ammonium bromide, the amino-acid (0·17 gram) gave α_{5461} +2·44°, $[\alpha]_{5461}$ +122°; that from the other solution (0·14 gram) gave α_{5461} 2·62°, $[\alpha]_{5461}$ +131°.

Liquid Ammonia.

A solution of 0·5 gram of the *l*-bromo-acid in 10 c.c. of liquid ammonia, kept in a sealed tube at 15° for eight days, gave as first crop 0·20 gram of amino-acid, α_{5461} −0·76°, $[\alpha]_{5461}$ −38°, and a very small second crop. The imino-acid (0·03 gram), $c=0·28$, had α_{5461} +0·90, $[\alpha]_{5461}$ +161°. In an exactly corresponding experiment, except that the solution contained also 2 grams of ammonium bromide and was kept for thirteen days, the first crop of amino-acid (0·264 gram) and also the small second crop were inactive. The

imino-acid (0·0036 gram) gave for $c=0\cdot036$ α_{5461} $+0\cdot34°$, $[\alpha]_{5461}$ + 198°. As, owing to the large amount of ammonium bromide in the second experiment, repeated washing of the first crop of amino-acid was necessary for purification, it cannot be affirmed that racemisation was quite complete, but in any case the activity of the amino-acid formed in these circumstances must be extremely small.

Methyl Alcohol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of methyl alcohol saturated with dry ammonia, kept for fifteen days at 15°, gave a first crop of amino-acid (0·12 gram) with α_{5461} $+0\cdot04°$, $[\alpha]_{5461}$ $+2°$, and a second crop (0·013 gram) which was quite inactive. The imino-acid (0·0025 gram) gave for $c=0\cdot025$ α^{15}_{5461} $+0\cdot09°$, $[\alpha]^{15}_{5461}$ $+180°$.

In an exactly corresponding experiment, except that the solvent was partly saturated with ammonia (3 c.c. of the solvent saturated with ammonia were added to 12 c.c. free from ammonia) and the solution kept for eighteen days at 15°; the first crop of amino-acid (0·077 gram) was inactive, the second crop (0·027 gram) gave for $c=0\cdot265$ α_{5461} $+0\cdot06$, $[\alpha]_{5461}$ $+11°$. The imino-acid (0·025 gram) gave for $c=0\cdot245$ α_{5461} $+0\cdot94°$, $[\alpha]_{5461}$ $+192°$.

The small yields of amino-acid are due to the simultaneous formation of phenylmethoxyacetic acid and (in the second experiment) to the fact that the reaction was incomplete.

Ethyl Alcohol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent saturated with dry ammonia, kept for fifteen days at 15°, gave a first crop of amino-acid (0·275 gram) having α_{5461} $+0\cdot04°$, $[\alpha]_{5461}$ $+2°$, and a second crop (0·02 gram) which was inactive. The imino-acid (0·081 gram) gave for $c = 0\cdot224$ α^{18}_{5461} $+0\cdot54°$, $[\alpha]^{18}_{5461}$ $+120\cdot5°$.

In a second exactly corresponding experiment, except that the solution was kept at 0° for ten days and at 20° for two days, the first crop of amino-acid (0·30 gram) gave α_{5461} $+0\cdot06°$, $[\alpha]_{5461}$ $+3°$; the second crop (0·012 gram) gave no measurable rotation. The imino-acid (0·028 gram), $c=0\cdot155$, gave α_{5461} $+0\cdot34°$, $[\alpha]_{5461}$ $+109°$.

The filtrate, after separation of the imino-acid, in the first experiment had a slight negative rotation, and in the second experiment was inactive, whereas in all other solvents the final filtrate had a slight activity corresponding in sign with the amino-acid. No satisfactory explanation of this result has been found. It is possible

that in ethyl alcohol traces of a lævorotatory compound are formed in such amount as to compensate, or in some cases over-compensate, the slight activity due to the amino-acid always present in traces in the final filtrate.

n-*Propyl Alcohol.*

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent, saturated with ammonia at 0° and kept at 15° for fifteen days, gave a first crop of amino-acid (0·24 gram) of α_{5461} +0·09, $[\alpha]_{5461}$ +4·6°, and a second crop (0·007 gram), which for c=0·07 gave α_{5461} +0·05°, $[\alpha]_{5461}$ +35·7°. The imino-acid (0·087 gram) gave for c=0·2 α_{5461} +0·75°, $[\alpha]_{5461}$ +187·5°.

iso*Propyl Alcohol.*

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent saturated with ammonia and kept for sixteen days at 15° gave a first crop of amino-acid (0·29 gram) of α_{5461} +0·05°, $[\alpha]_{5461}$ +2·5°, and a second crop, which for c=0·127 gave α_{5461} +0·05°, $[\alpha]_{5461}$ +19·7°. The imino-acid (0·081 gram) gave for c=0·17 α_{5461} +0·59°, $[\alpha]_{5461}$ +173·5°.

n-*Butyl Alcohol.*

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent (b. p. 117°), saturated with ammonia and kept for twelve days at 15°, gave a first crop of amino-acid (0·22 gram) of α^{18}_{5461} +0·25°, $[\alpha]^{18}_{5461}$ +12·5°, and a second crop (0·009 gram) gave for c=0·09 α_{5461} +0·18°, $[\alpha]_{5461}$ +147°. The imino-acid (0·1 gram, m. p. 208° decomp.) gave for c=0·17 α^{17}_{5461} +0·70°, $[\alpha]^{17}_{5461}$ +206°. The readings for the first and third crops were repeated after a lapse of three months; the values found were +0·24° and +0·68° respectively, so that the activity of both acids remains practically unaltered by keeping in *N*-hydrochloric acid solution.

Trimethylcarbinol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of the solvent saturated with ammonia at 0° and kept for twenty-five days at 15° gave a first crop of amino-acid (0·17 gram) of α_{5461} +0·08°, $[\alpha]_{5461}$ +4°, and a second crop (0·0275 gram), which for c=0·275 gave α^{16}_{5461} +0·74°, $[\alpha]^{16}_{5461}$ +134·5°. The imino-acid (0·12 gram—the largest proportion in any solvent) gave for c=0·15 α_{5461} +0·58°, $[\alpha]_{5461}$ +193°.

n-Heptyl Alcohol.

A solution of 0·75 gram of the *l*-bromo-acid in 15 c.c. of solvent (b. p. 174—176°) saturated at 0° with ammonia and kept for sixty-two days at 15° gave a first crop of amino-acid (0·12 gram) of α_{5461} +2·51°, $[\alpha]_{5461}$ +125·5°, and a second crop (0·0173 gram), which for c=0·173 gave α_{5461} +0·55°, $[\alpha]_{5461}$ +159°. The imino-acid (0·058 gram) gave for c=0·165 α_{5461} +0·56°, $[\alpha]_{5461}$ +170°.

Acetonitrile.

0·75 Gram of the *l*-bromo-acid was dissolved in 15 c.c. of the solvent and ammonia passed in at 0°. A white, flocculent precipitate appeared almost immediately, and when the solution was saturated, the tube contained a voluminous, white paste which, on keeping in the ice-chest overnight, set to a jelly. It was kept at 55° for a few days, but on showing no change it was kept at the ordinary temperature for a further ninety days. Gradually the jelly gave place to a white, flocculent precipitate contained in a mobile liquid (compare Senter and Drew, *loc. cit.*, p. 1101). The first crop of amino-acid (0·375 gram), separated from this precipitate in the ordinary way, gave α_{5461} −0·71°, $[\alpha]_{5461}$ −35·5°. The second crop (0·044 gram) gave for c=0·432 α_{5461} −1·37°, $[\alpha]_{5461}$ −158·5°. The imino-acid (0·012 gram), which separated in small, cubical crystals, unlike the clusters of needles obtained from all other solvents, gave for c=0·12 α_{5461} +0·16°, $[\alpha]_{5461}$ +66·7°, and was probably contaminated with some *l*-phenylaminoacetic acid.

Summary.

(1) The amino-acid obtained by the action of ammonia on optically active phenylbromoacetic acid in different solvents is opposite in sign to the bromo-acid when water and certain alcohols are used, but similar in sign to the bromo-acid when liquid ammonia and acetonitrile are employed as solvents.

(2) The amino-acid from the lower aliphatic alcohols as solvents is more racemised than that from the higher alcohols.

(3) The presence of ammonium bromide has little effect on the activity of the amino-acid from aqueous ammonia; it has a great racemising effect when the reaction is carried out in liquid ammonia.

(4) Iminodiphenyldiacetic acid is formed in small quantity in all the solvents used; in all cases it is highly active and of opposite sign to the original bromo-acid.

(5) The mechanism of the formation of the imino-acid is discussed.

We desire to thank the Government Grant Committee of the Royal Society for a grant which has defrayed the expenses of this investigation.

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[*Received, February 4th*, 1918.]

XVIII.—*Studies on the Walden Inversion. Part VII. The Influence of the Solvent on the Sign of the Product in the Conversion of α-Bromo-β-phenylpropionic Acid to α-Amino-β-phenylpropionic Acid (Phenylalanine). Iminodiphenyldipropionic Acid.*

By GEORGE SENTER, HARRY DUGALD KEITH DREW, and GERALD HARGRAVE MARTIN.

IN previous papers (Senter and Drew, T., 1915, **107**, 638; 1916, **109**, 1091; Senter and Tucker, this vol., 140) it has been shown that when the halogen atom in phenylchloro- and phenylbromo-acetic acid is displaced by the amino-group by the direct action of ammonia, the optical sign of the resulting amino-acid depends on the nature of the solvent in which the reaction occurs. In the case of the bromo-acid (Senter and Tucker, *loc. cit.*), the amino-acid obtained from liquid ammonia and from acetonitrile has the same sign as the bromo-acid taken, whereas from the other solvents an amino-acid of the opposite sign to the original bromo-acid is produced.

In both the acids referred to the phenyl group is directly attached to the asymmetric carbon atom, and in order to find how the results would be affected by a phenyl group further from the point at which substitution occurs, a similar investigation has now been carried out with α-bromo-β-phenylpropionic acid (benzylbromoacetic acid), $C_6H_5 \cdot CH_2 \cdot CHBr \cdot CO_2H$, and the results are described in the present paper.

The acid was resolved by a slight modification of the method described by Fischer and Carl (*Ber.*, 1906, **39**, 4000); the most

active specimens gave for $[\alpha]_D^{17}$ the value $-10{\cdot}2°$, as compared with $[\alpha]_D^{20}$ $-8{\cdot}3°$, the highest value obtained by Fischer and Carl. Most of the measurements were made with two preparations of the *l*-acid of activity $[\alpha]_D^{17}$ $-8{\cdot}8°$ and $-10{\cdot}2°$ respectively; in a few cases, a dextrorotatory acid of lower activity was used.

The main reaction between ammonia and the ammonium salt of the bromo-acid proceeds according to the equation

$$CH_2Ph{\cdot}CHBr{\cdot}CO_2{\cdot}NH_4 + NH_3 \longrightarrow CH_2Ph{\cdot}CH(NH_2){\cdot}CO_2H + NH_4Br,$$

but in all the solvents a certain proportion of cinnamic acid, $CHPh{:}CH{\cdot}CO_2H$, is formed by elimination of hydrogen bromide. Further, an imino-acid, which is shown to be *α-imino-ββ-diphenyldipropionic acid*, $CH_2Ph{\cdot}CH(CO_2H){\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph$, was isolated from the products of reaction in all the solvents used. This imino-acid, which has not hitherto been described, may be regarded as being formed by the interaction of two molecules of the ammonium salt and one molecule of ammonia, according to the equation

$$2CH_2Ph{\cdot}CHBr{\cdot}CO_2{\cdot}NH_4 + NH_3 \longrightarrow CH_2Ph{\cdot}CH(CO_2H){\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph + 2NH_4Br.$$

The method used in isolating the amino-acid in a pure condition, and the identification and properties of the imino-acid, are fully described in the experimental portion of the paper. The reaction in all cases took place at the ordinary temperature, and as the halogen in this case is much less reactive than in phenylbromoacetic acid (compare Senter and Martin, T., 1917, **111**, 447), the reacting substances were kept in sealed tubes for two or three weeks in the case of liquid and aqueous ammonia and acetonitrile, and for some months in the case of the alcohols, in order to ensure that the changes were practically complete.

The optical activity of the products was determined for the mercury green ($\lambda = 5461$) as well as for sodium light. The measurements with phenylalanine were made in aqueous solution, the concentration in all cases except one (product from benzonitrile, $c = 0{\cdot}646$) being about 1 per cent. ($c = 1{\cdot}0$). The measurements with the imino-acid, on account of its very sparing solubility in water and in dilute hydrochloric acid (p. 162), were made in $1{\cdot}082 \times N/20$-sodium hydroxide. Owing to the small yields of the imino-acid from certain solvents, very dilute solutions had in some cases to be used for the activity measurements, and it was therefore not convenient to make up the solutions to the same concentration, as in the case of the amino-acid. The main results of the investigation are summarised in table I.

TABLE I.

Solvent.	Value of $[\alpha]_D^{17}$ for bromo-acid used.	Value of $[\alpha]_D^{17}$ for phenyl-alanine.	Value of $[\alpha]_{5461}$ for imino-acid
Water (35 per cent. NH_3) ...	$-8.8°$	$+26°$	$-34°$ ($c = 0.292$)
Water + NH_4Br	-8.8	$+27$	
Liquid ammonia	-8.8	$+10$	
,,	-10.2	$+7$	
Liquid Ammonia + NH_4Br.........	-8.8	$+25$	
	-10.2	$+30$	
$CH_3{\cdot}CN$	-8.8	$+9$	
,, ...	$+5.8$	-8	$+11$ ($c = 1.10$)
$C_6H_5{\cdot}CN$	$+6.2$	-7	
$CH_3{\cdot}OH$	-8.8	$+23$	-34 ($c = 0.219$)
$C_2H_5{\cdot}OH$	-8.8	$+25$	-35 ($c = 0.542$)
$C_3H_7{\cdot}OH$ (n) ...	-8.8	$+24$	-34 ($c = 0.591$)
$C_4H_9{\cdot}OH$ (n) ...	-8.8	$+19$	-33 ($c = 0.458$)
$(CH_3)_3C{\cdot}OH$ ...	-8.8	$+22$	-28 ($c = 0.909$)
$C_6H_5{\cdot}CH_2{\cdot}OH$ ...	$+6.2$	practically inactive.	$+30$ ($c = 0.168$)

The value $[\alpha]_D^{16}$ for pure *d*-phenylalanine in 2·03 per cent. aqueous solution is $+35.1°$ (Fischer and Mouneyrat, *Ber.*, 1900, **33**, 2383).

Although, owing to its solubility in water, the amino-acid cannot be isolated quantitatively from the products of reaction, there is no doubt that the numbers given in the table represent fairly accurately the relative activities of the products from the different solvents. As the solubility of the inactive acid is considerably less than that of the active acid (p. 159), a greater proportion of the latter will, as a rule, be removed during the washing of the products with water, and therefore the numbers in the table must be rather lower than those for the amino-acid formed. The yields of phenylalanine from the solutions in benzonitrile and in benzyl alcohol are so small (0·07 and 0·06 gram respectively) that not much confidence can be placed in the results from a quantitative point of view, as the active acid would be largely removed during washing with water.

Fischer and Carl (*loc. cit.*), by the action of aqueous ammonia on a bromo-acid of activity $[\alpha]_D^{20}$ -8.3, obtained phenylalanine with $[\alpha]_D^{20}$ $+31.78°$. The slightly higher value as compared with ours is probably to be accounted for partly by a difference in the amount of washing and partly by the fact that they carried out the early stages of the reaction at a very low temperature.

The formation of an imino-acid in the reaction was overlooked by Fischer and Carl.

Discussion of Results.

The main result of the investigation, so far as the formation of amino-acid is concerned, is that with all the ten solvents used the amino-acid obtained has the same sign, opposite to that of the bromo-acid taken. Further, except in the case of solutions in liquid ammonia, acetonitrile, and benzonitrile, the displacement of bromine by NH_2 takes place without marked racemisation; for reasons already given, the racemisation is even less than appears from the numbers in the table. The effect of ammonium bromide (about 4 grams in 15 c.c.) on the reaction was examined, with remarkable results. Whereas this salt has practically no influence on the activity of the amino-acid obtained from aqueous ammonia, it greatly diminishes the racemisation of the product from liquid ammonia (p. 160).

It is instructive to compare these results with those obtained with phenylbromoacetic acid, as the two acids differ mainly as regards the relative position of the phenyl group with reference to the asymmetric carbon atom (or to the bromine atom). With phenylbromoacetic acid, racemisation was pronounced in all solvents; the amino-acid from liquid ammonia and from acetonitrile had the same sign as the original bromo-acid, whereas in all other solvents it had the opposite sign; finally, whereas ammonium bromide had little effect on the activity of the amino-acid from aqueous ammonia, it produced complete racemisation as regards the amino-acid from liquid ammonia. At first sight there does not seem to be much resemblance in the behaviour of the two acids towards ammonia, but a little consideration puts the matter in a different aspect. The most significant fact appears to be that the phenylalanine from liquid ammonia and from acetonitrile is racemised to a greater extent than that from other solvents, and it is just in those two solvents that the action of ammonia on phenylbromoacetic acid yields an amino-acid opposite in sign to that obtained from all the other solvents. This is most readily accounted for on the assumption that, as compared with other solvents, these two solvents favour the formation of an amino-acid of the same sign as the original bromo-acid, but whereas with *l*-α-bromo-β-phenylpropionic acid the result is the formation of a considerable proportion of both *d*- and *l*-phenylalanine, the product as a whole being dextrorotatory, with *l*-phenylbromoacetic acid the tendency to the formation of the *l*-amino-acid is so much greater that the product as a whole is lævorotatory.

The remarkable effect of ammonium bromide on the two reactions in liquid ammonia can be represented on similar lines; the assump-

tion in this case is that the salt favours the production of an amino-acid having the opposite sign to that of the original bromo-acid. In the case of *l*-α-bromo-β-phenylpropionic acid, the result is a diminution in the racemisation of the resulting *d*-phenylalanine, whilst with *l*-phenylbromoacetic acid, the resulting amino-acid is practically inactive as compared with the formation of a lævorotatory acid in the absence of the salt. It appears justifiable, therefore, to draw the conclusion that the same solvents produce similar effects, of different magnitudes, on the action of ammonia on the active phenylbromoacetic and phenylbromopropionic acids. This conclusion receives strong support from the fact, established in a recent paper (Senter and Martin, T., 1917, **111**, 447), that there is a close analogy in the action of water on the two acids and on their sodium salts.

The same considerations apply to the results with the different alcohols as solvents. The tendency to the formation of an amino-acid of the same sign as that of the original bromo-acid is so much greater in the case of phenylbromoacetic acid that whereas the *d*-phenylalanine from *l*-bromo-β-phenylpropionic acid is scarcely racemised, the amino-acid from *l*-phenylbromoacetic acid, although dextrorotatory, is in most cases only slightly active. In the same circumstances, *l*-phenylchloroacetic acid yields an amino-acid which is slightly lævorotatory.

These results are perhaps best accounted for on the hypothesis that the action of ammonia on the halogen-substituted acids proceeds as two simultaneous reactions, giving rise to *d*- and *l*-amino-acids respectively; for example,

$$l\text{-phenylbromoacetic acid} \begin{cases} \longrightarrow d\text{-phenylaminoacetic acid} \\ \longrightarrow l\text{-phenylaminoacetic acid,} \end{cases}$$

and that one or the other action predominates, depending on the nature of the halogen acid, the nature of the solvent, and other conditions. The nature of these reactions will be discussed when fuller experimental data are available.

The investigations of Franklin and Kraus (*J. Amer. Chem. Soc.*, 1905, **27**, 191) furnish an interesting analogy to the slight influence of ammonium haloids on the effect of aqueous ammonia as compared with liquid ammonia in the reactions just discussed. Both liquid ammonia and aqueous ammonia react with mercuric chloride as follows:

$$HgCl_2 + 2NH_3 \longrightarrow HgCl_2,2NH_3 \longrightarrow NH_2{\cdot}HgCl + NH_4Cl.$$

In liquid ammonia, the presence of a small quantity of ammonium

chloride prevents the formation of the ammono-basic salt ($NH_2 \cdot HgCl$), whilst in aqueous ammonia a large excess of ammonium chloride is necessary to ensure a pure precipitate of the compound $HgCl_2,2NH_3$.

The above considerations throw some light on the question of the occurrence of racemisation in reactions involving displacement of groups, a subject about which very little is known. This type of racemisation is quite distinct from catalytic racemisation; for example, the conversion of active to inactive mandelic acid by heating with alkali. Catalytic racemisation has in some cases been satisfactorily accounted for on the basis of the formation of intermediate compounds not containing an asymmetric carbon atom (compare Werner, "Stereochemie," p. 52; Lowry, *Rep. Brit. Assoc.*, 1904; McKenzie and Widdows, T., 1915, **107**, 704), and an explanation on similar lines may be found applicable in some cases of displacement racemisation. The results described in this paper, however, make it probable that the racemisation accompanying the displacement of the halogen atom in the phenylhalogenacetic acids is due to the occurrence of two simultaneous reactions, resulting in the formation of *d*- and *l*-amino-acids respectively, and this explanation will probably be found applicable to other examples of displacement racemisation.

With the further data now available, the interconversion of the halogen and amino-derivatives of the two acids in question can be summarised as follows (compare Fischer and Carl, *loc. cit.*; McKenzie and Clough, T., 1909, **95**, 777; Frankland, T., 1913, **103**, 731):

d-Phenylalanine $\xrightarrow{NOBr}$

d-α-bromo-β-phenylpropionic acid $\xrightarrow[\text{aqueous } NH_3]{\text{liq. } NH_3}$ *l*-phenylalanine.

d-Phenylglycine $\xrightarrow{NOCl}$

l-phenylchloroacetic acid $\xrightarrow{\text{liq. } NH_3}$ *l*-phenylglycine.

$\xrightarrow{\text{aqueous } NH_3}$ *d*-phenylglycine.

These results are very puzzling, and there appears to be little advantage in discussing them more fully until further information as to the mechanism of the reactions involved has been obtained. These investigations are now in progress.

It may be mentioned that Werner, in the course of his investigations on stereoisomeric cobalt compounds (*Annalen*, 1912, **386**, 57), has found that the displacement of a halogen atom in the inner sphere by the NH_3-group takes place more often abnormally than normally (that is, a *cis*-compound is usually obtained from a

trans-, and vice versa), and this is the case both with liquid ammonia and aqueous ammonia as substituting agents.

α-Imino-ββ-diphenyldipropionic Acid.—In the case of the *l*-phenylhalogenoacetic acids (Senter and Drew, *loc. cit.*; Senter and Tucker, *loc. cit.*), it was shown that the action of ammonia in all the solvents examined produced an imino-acid which was dextrorotatory in *N*-hydrochloric acid solution. The imino-acid produced by the action of ammonia on *l*-α-bromo-β-phenylpropionic acid in all the solvents examined is lævorotatory in *N*/20-sodium hydroxide solution. The latter imino-acid is not sufficiently soluble in *N*-hydrochloric acid to be examined in this solvent, but phenyliminoacetic acid was shown to be dextrorotatory in both *N*-hydrochloric acid and *N*/20-sodium hydroxide; thus, a specimen having $[\alpha]^{17}_{5461}$ +190° in *N*-hydrochloric acid ($c = 0{\cdot}15$) gave $[\alpha]^{17}_{5461}$ +167° in 1·082*N*/20-sodium hydroxide ($c = 0{\cdot}09$). The nature of the solvent is therefore without influence on the sign of the resulting imino-acid in the case of the two acids in question. The theoretical bearing of these results is briefly discussed in the preceding paper (Senter and Tucker, this vol., p. 145).

It is clear from the graphic formula of α-imino-ββ-diphenyldipropionic acid (p. 152) that optical inactivity may be due either to the presence of equal amounts of the *d*- and *l*-acid or to internal compensation. The fact that the melting point of the partly active imino-acid is close to and a few degrees below that of the inactive acid obtained from *r*-α-bromo-β-phenylpropionic acid would accord with the view that the latter acid is the racemic form, but this argument is, of course, not conclusive.

EXPERIMENTAL.

Resolution of r-*α-Bromo-β-phenylpropionic Acid.*

The pure *r*-acid was prepared by Fischer's method (compare Senter and Martin, T., 1917, **111**, 447), and was resolved with brucine by a modification of the method of Fischer and Carl (*loc. cit.*), which consisted in redissolving the precipitated brucine salt at the ordinary temperature in a mixture of alcohol and water (in which it is more readily soluble than in either of the pure solvents) instead of in alcohol at 25° (Fischer and Carl). The details of one experiment are as follows. Thirty grams of the *r*-bromo-acid were dissolved in 150 c.c. of alcohol, and 51·5 grams of anhydrous brucine added, with shaking, at 16°. The solution was filtered, and 900 c.c. of water were added, with stirring. An oil was deposited, which solidified after twenty-four hours. The solid, after being collected

and dried, weighed 53 grams. It was redissolved in a mixture of 250 c.c. of alcohol and 50 c.c. of water, and the solution poured into 1600 c.c. of water. The dried salt finally obtained weighed 26 grams. The acid prepared from it by decomposing with dilute hydrochloric acid and extracting with ether had $\alpha_D^{18} - 13{\cdot}06°$ for $l = 1$, corresponding with $[\alpha]_D^{18} - 8{\cdot}80$, and contained the theoretical proportion of bromine. The acid obtained from the first mother liquor was a yellow oil, which gradually deposited a little of the solid *r*-acid. The remainder gave for $\alpha_D^{18} + 8{\cdot}54°$, $l = 1$.

In another experiment, in which the brucine salt was three times crystallised, the acid gave α_{5461}^{17} $-19{\cdot}14°$ and $\alpha_D^{17} - 15{\cdot}22°$ for $l = 1$. The density of the liquid was found to be 1·487 at 17° and 1·479 at 25°; hence $[\alpha]_{5461}^{17}$ is $-12{\cdot}9°$ and $[\alpha]_D^{17}$ $-10{\cdot}2°$. In order to obtain a comparison with Fischer's measurements at 20°, the effect of change of temperature on the rotation of another specimen was determined, with the following results: $\alpha_{5461}^{17{\cdot}5} - 16{\cdot}92°$, α_{5461}^{25} $-17{\cdot}52°$, $\alpha_{5780}^{17{\cdot}5}$ $-14{\cdot}28°$, α_{5780}^{25} $-14{\cdot}86°$ for $l = 1$. The rotation of α-bromo-β-phenylpropionic acid therefore increases markedly with rise of temperature. The value of $[\alpha]_D$ for our most active specimen at 20° was therefore about $-10{\cdot}4°$, as compared with $-8{\cdot}3°$ for the purest acid of Fischer and Carl. Even after prolonged keeping in a vacuum, our acid could not be obtained in the solid form, so it was probably not quite optically pure.

Method of Experiment.

The method of experiment was similar to that already employed in the case of phenylchloroacetic acid (T., 1916, **109**, 1098). About 1 gram of the bromo-acid was dissolved in about 15 c.c. of the solvent, the solution saturated with dry ammonia, sealed up in a Jena-glass tube, and left at the ordinary temperature until the change was assumed to be complete. The solvent and excess of ammonia were then evaporated off at as low a temperature as possible (in some cases under diminished pressure), the residue was dissolved in water, made acid to Congo-red by addition of hydrochloric or hydrobromic acid, and the precipitate, consisting of the bulk of the imino-acid and cinnamic acid, collected and washed with cold water. From the precipitate, the pure imino-acid was isolated by extracting the cinnamic acid with ether.

The slightly acid aqueous filtrate containing the amino-acid, any unchanged bromo-acid, any hydroxy-acid or alkyloxy-acid formed in the course of the reaction, together with traces of imino-acid and cinnamic acid, was repeatedly extracted with ether, whereby all but the amino-acid and remaining imino-acid were removed. The

amino-acid was then freed from imino-acid and from ammonium chloride and bromide by evaporating the solution to dryness, dissolving in aqueous ammonia, again evaporating to dryness, and finally treating with small quantities of cold water until the filtrate was free from halogen salts. In this way, any remaining imino-acid was removed, since its ammonium hydrogen salt is stable and soluble in cold water.

The purity of the amino-acid was checked by determining its equivalent as hydrochloride, as described for phenylaminoacetic acid, and as in all cases practically theoretical results were obtained, it is unnecessary to quote the actual figures. In some cases the proportion of nitrogen was estimated by combustion.

As regards the different solvents, the results obtained with liquid ammonia, aqueous ammonia, and acetonitrile are of fundamental importance for the question of the replacement of halogen atoms by the amino-group, and the details of the experiments are therefore briefly summarised. As the remaining solvents, comprising a number of alcohols, all give very similar results, it seems unnecessary to describe the experiments in detail.

Aqueous Ammonia.

The velocity of reaction between inactive α-bromo-β-phenylpropionic acid and aqueous ammonia (35 per cent. NH_3) was determined approximately at 25°. From a solution containing 1·22 grams of the acid in 50 c.c. of the solution, about half the bromine was displaced in twenty-four hours. In a corresponding experiment with ethyl alcohol saturated with ammonia at 25°, about half the bromine was displaced in fourteen days.

In a preliminary experiment, in which 3 grams of the *r*-acid in 20 c.c. of aqueous ammonia (35 per cent. NH_3) was kept for seven days at 25°, 1·1 grams of pure *r*-phenylalanine and 0·1 gram of the imino-acid were obtained. The saturated solution of *r*-phenylalanine in water at 12° contains 1·24 grams in 100 c.c. of solution, about half that given by Fischer and Mouneyrat (*loc. cit.*) for the pure active forms.

A solution of 1·02 grams of *l*-α-bromo-β-phenylpropionic acid in 22 c.c. of aqueous ammonia (35 per cent. NH_3), kept for forty-two days at the ordinary temperature, gave 0·45 gram of amino-acid, $[\alpha]_D^{15} + 24°$ (m. p. 258—259° decomp.; rapid heating). In another experiment, 0·77 gram of the *l*-bromo-acid in dilute aqueous ammonia (4 per cent. NH_3), kept for twenty-one days at the ordinary temperature, yielded only 0·09 gram of amino-acid, $[\alpha]_D^{16} + 17°$. From the ethereal solution (compare the method of

experiment), crystals were obtained which, after recrystallisation from benzene, melted at 123—125° and gave in ethyl alcohol $[\alpha]_{5461}^{16\cdot5}$ $-21\cdot5°$, $c = 0\cdot373$. The substance is evidently nearly pure *l*-α-hydroxy-β-phenylpropionic acid, formed by the action of water on the ammonium salt of the bromo-acid: It has been shown by McKenzie and Wren (T., 1910, **97**, 1355) that *l*-α-bromo-β-phenylpropionic acid gives a hydroxy-acid of the same sign when acted on by water, by aqueous sodium hydroxide, by water and calcium carbonate, and by water and silver oxide.

The effect of ammonium bromide on the activity of the resulting phenylalanine was determined as follows. A solution of 1·02 grams of the *l*-bromo-acid, $[\alpha]_D^{17} - 8\cdot8°$, and 4 grams of ammonium bromide in 22 c.c. of aqueous ammonia (35 per cent. NH_3) was kept for eleven days at the ordinary temperature. The yield of phenylalanine was 0·27 gram of $[\alpha]_D^{15} + 27°$, which is practically the same as that obtained in the absence of ammonium bromide.

Liquid Ammonia.

A solution of 0·53 gram of the *l*-bromo-acid, $[\alpha]_D^{17} - 8\cdot8°$, in 16 c.c. of liquid ammonia, kept for fourteen days, gave 0·17 gram of amino-acid, $[\alpha]_D^{14} + 8\cdot5°$. 0·85 Gram of the *l*-bromo-acid, $[\alpha]_D^{17} - 8\cdot8°$, and 4 grams of ammonium bromide, dissolved in 13 c.c. of liquid ammonia and kept for fourteen days, gave 0·1 gram of amino-acid, $[\alpha]_D^{17} + 24\cdot5°$. It appears from these data that in the presence of ammonium bromide the resulting phenylalanine is racemised to a much smaller extent than in the absence of the salt. In order to place this important result beyond doubt, two exactly parallel experiments were carried out, as follows. Two tubes, each containing 0·86 gram of the *l*-bromo-acid, $[\alpha]_D^{17} - 10\cdot2°$, in 13 c.c. of liquid ammonia, and one containing 4 grams of ammonium bromide in addition, were kept for fourteen days. The ammonia was then allowed to evaporate, the residue in each case dissolved in water and made up to 50 c.c., and 4 grams of ammonium bromide were added to the solution which did not already contain the salt. The amino-acid was then isolated in the usual way. From the solution originally containing ammonium bromide, the yield of amino-acid was 0·12 gram, $[\alpha]_D^{19} + 30°$. From the corresponding solution without ammonium bromide the yield of amino-acid was 0·14 gram, $[\alpha]_D^{19} + 6\cdot5°$, so that the previous result was fully confirmed.

Acetonitrile.

A solution of 1·08 grams of the *l*-bromo-acid, $[\alpha]_D^{16}$ $-8·8°$, in 15 c.c. of acetonitrile was saturated with dry ammonia at 9°, whereby the volume increased by 1·2 c.c. The solution at first was clear, but a precipitate consisting of the ammonium salts of the amino-acid, the imino-acid, and cinnamic acid soon began to form. After twenty-four days, the precipitate was collected, and the amino-acid obtained as usual, the yield being 0·2 gram, $[\alpha]_D^{14}$ $+9°$. The imino-acid was accidentally lost.

A second experiment with a less active bromo-acid ($[\alpha]_D^{18}$ $+5·8°$) in more concentrated solution (3·9 grams in 17 c.c. of solvent), kept for twenty-one days, gave 0·35 gram of (recrystallised) phenylalanine, $[\alpha]_D^{20}$ $-8°$, and 0·57 gram of imino-acid (compare the section on the imino-acid). It appears therefore that, as would be anticipated, the more concentrated the solution of bromo-acid the greater is the yield of imino-acid.

The Alcohols.

As the reaction in these solvents is very slow, the solutions were kept for 280—300 days before separating the products. In each case, 0·7—0·8 gram of active bromo-acid was used, and the yield of amino-acid (except with benzyl alcohol) varied from 0·15—0·25 gram. With methyl alcohol, the solutions remained clear throughout, showing that the amino-acid and imino-acid (or their ammonium salts) are soluble in this solvent. With the other alcohols, except benzyl alcohol, a small amount of precipitate formed after a time. The absence of a precipitate in the benzyl alcohol solution is probably due to the slow rate of reaction in this solvent, as only 0·06 gram of amino-acid and 0·02 gram of imino-acid were obtained, although the mixture was kept for 309 days. The relative activities of the amino-acids from the different solvents are given in the table. The properties of the partly active imino-acids obtained from these solvents are briefly dealt with in the next section.

α-Imino-ββ-diphenyldipropionic Acid.

As this acid has not been previously obtained, it is desirable to describe its properties in some detail. Earlier experiments having shown that a good yield of the imino-acid was obtained from acetonitrile, 8·4 grams of the *r*-bromo-acid were dissolved in 20 c.c. of

this solvent, the solution being saturated with dry ammonia and kept for twenty-eight days. The precipitate was then collected, washed with ether, and the inactive imino-acid separated as already described (p. 158). After crystallisation from a mixture of acetone and water, in which it is very sparingly soluble, the compound forms stellar aggregates of elongated leaflets or needles melting and decomposing at 262—264°, with previous discoloration and shrinkage at 235°. Before analysis, it was dried for some hours at 100°:

0·2588 gave 0·6545 CO_2 and 0·1447 H_2O. C=69·0; H=6·27.
0·5561 ,, 21·1 c.c. N_2 (moist) at 18° and 771 mm. N=4·5.
$C_{18}H_{19}O_4N$ requires C=69·0; H=6·1; N=4·5 per cent.

α-Imino-ββ-diphenyldipropionic acid is very sparingly soluble in water, practically insoluble in dilute or concentrated hydrochloric acid, but readily soluble in dilute alkali hydroxide solution. This shows that, as would be anticipated, it is an extremely weak base, whereas its acidic character is fairly pronounced. An attempt to determine its equivalent by evaporating with hydrochloric acid gave an unsatisfactory result, as the hygroscopic hydrochloride decomposed on drying at 100°. Further, no definite results for the equivalent were obtained by titration, using phenolphthalein as indicator, or by evaporating with ammonia, in an attempt to prepare a pure ammonium salt. Evidence was obtained in some of the experiments with acetonitrile as to the dibasic character of the acid, since the solid imino-acid compound which separates from this solvent during the reaction, on treatment with water in the cold, gives off ammonia, forming an ammonium salt (the hydrogen ammonium salt) soluble in water.

The amount of active imino-acid obtained from most of the solvents was very small, on the average 0·05 gram (from trimethylcarbinol 0·1 gram), but the rotation measurements were quite definite. The various specimens decomposed on heating to 245—251°.

Summary.

(1) The amino-acid obtained by the action of ammonia on optically active α-bromo-β-phenylpropionic acid in different solvents has in all cases the same sign, opposite to that of the original bromo-acid.

(2) The amino-acid from liquid ammonia and acetonitrile is more racemised than that from other solvents.

(3) The presence of ammonium bromide has little effect on the

activity of the product from aqueous ammonia; it greatly diminishes the racemisation when the reaction is carried out in liquid ammonia.

(4) α-Imino-$\beta\beta$-diphenyldipropionic acid was isolated from the products of reaction in all solvents used, and its properties were investigated; the sign was in all cases the same as that of the original bromo-acid.

(5) The mechanism of displacement racemisation is discussed.

In conclusion, we desire to thank the Government Grant Committee of the Royal Society for a grant which has defrayed the expenses of this investigation.

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[*Received, February 4th,* 1918.]

XIX.—*The Action of Aniline on Carbon Tetrachloride.*

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THE action of aniline on carbon tetrachloride was studied long ago by Hofmann (*Proc. Roy. Soc.*, 1858, **9**, 284). He found that no action was apparent at the ordinary temperature, but that, on heating 3 volumes of aniline with 1 volume of carbon tetrachloride in a sealed tube for thirty hours at 170—180°, a soft, black mass was obtained, from which he prepared pararosaniline and a new base, diphenylaminobenzamidine (carbotriphenyltriamine), $C_{19}H_{17}N_3$. He also obtained the hydrochloride of this substance, but did not pursue his researches further. Weith (*Ber.*, 1877, **10**, 358) many years afterwards attacked the problem of the structure of the base. He prepared it by Hofmann's method, and succeeded in showing (*Ber.*, 1879, **12**, 101) that the constitution could be represented as

$$C_6H_5\cdot N\colon C{<}{\begin{matrix}NH\cdot C_6H_5\\ C_6H_4\cdot NH_2\end{matrix}}.$$

Later syntheses of diphenylaminobenzamidine (Michler and Walder, *Ber.*, 1881, **14**, 2174) confirmed the constitution thus established. The base is a product of the condensation of aniline with carbon tetrachloride, the latter supplying the central carbon atom. It is interesting in that the chlorine atoms of the tetrachloride have been displaced in three different ways: two chlorine

atoms have reacted with the two aminic hydrogen atoms in one aniline molecule, another has reacted with one aminic hydrogen atom in a second aniline molecule, and the fourth halogen atom has reacted with one of the ring hydrogen atoms in the para-position.

The present paper is the outcome of some experiments on the reaction in the presence of a catalyst. During the course of certain other work, it was noticed that a mixture of pure aniline and pure carbon tetrachloride, colourless at first, rapidly darkened at the laboratory temperature when in contact with a copper–mercury couple, ultimately becoming almost solid. As the reaction appeared to be far more rapid than that studied by Hofmann, it was of interest to discover whether the same products were formed. With this end in view, mixtures of aniline and carbon tetrachloride were allowed to react under varying conditions, and the main products were investigated.

EXPERIMENTAL.

Mixture 1.—A mixture of 3 molecular proportions of pure aniline and 1 molecular proportion of pure carbon tetrachloride was placed in contact with a copper–mercury couple and allowed to remain in a closed vessel until solid; this required three days at the ordinary temperature. Repeated extraction of the resulting black, oily substance with hot water showed that much of the original mixture was still unchanged. A tenacious black tar remained which solidified, on cooling, to a brittle, shining solid.

The brownish-red filtrate was boiled until all odour of aniline had disappeared, decolorised with animal charcoal, and set aside to crystallise. The crystals were purified by repeated crystallisation from water, and were then obtained quite clean and white, melting at 279° (291° corr.). This melting point agrees with that of the diphenylaminobenzamidine hydrochloride obtained by Weith. The presence of ionisable chlorine was shown by precipitation with silver nitrate; the base itself was prepared by the action of dilute sodium hydroxide solution on the salt and repeated crystallisation of the product from alcohol. It formed soft, creamy-white needles melting at 197° (203° corr.). (Found: C=79·10; H=6·16. $C_{19}H_{17}N_3$ requires C=79·40; H=5·97 per cent.) The substance was thus undoubtedly diphenylaminobenzamidine.

The black solid separated earlier was suspended in water and distilled in a current of steam. The distillate had a strong odour of phenylcarbylamine and deposited orange, crystalline scales.

These, after separation and purification, were shown to be azobenzene by their melting point, reactions, and quantitative analysis. A few drops of phenylcarbylamine were separated from the filtrate by extraction with ether.

Mixture 2.—This mixture was the same in composition as the previous one, and was heated at 80—90° with the copper-mercury couple under a reflux condenser for fifty minutes, when the mass had the appearance of moist black sand. Repeated extraction with hot water left only a small amount of dark, sooty material behind. The brown filtrate contained some aniline and azobenzene, and was boiled until these were removed. On crystallisation, much diphenylaminobenzamidine hydrochloride was again obtained. The red mother liquor, containing undoubtedly some pararosaniline hydrochloride, was evaporated, but the red colour was gradually destroyed, and only a further amount of the salt previously obtained and some aniline hydrochloride were found.

It was noticed that the diphenylaminobenzamidine salt obtained from this mixture had a persistent pale yellow colour, in spite of attempts to remove it by means of animal charcoal. Further, the corresponding salt from Mixture 1, which was pure white, became yellow on firm rubbing against the side of the porcelain dish with a glass rod, but ultimately became white again after some days. These changes could be induced repeatedly, so that apparently two modifications of the salt exist. On determining the melting point, the substance turns yellow at about 230°, and this colour increases until melting at 279° (291° corr.) takes place to a red liquid with partial decomposition.

Mixture 3.—This was a mixture of about equal parts of aniline and carbon tetrachloride, part of which was the middle fraction in the separation of the two liquids by fractional distillation. It was allowed to remain for several months without heating and in the absence of the catalyst. At intervals of a few weeks, the crystals which had formed in the dark brown liquid were collected and the filtrate was returned to the bottle. In each case, the substance obtained was treated as follows: The felted, hair-like mass was pressed in absorbent paper, extracted with water, and the extract allowed to crystallise. When crystals appeared, they were purified and identified as diphenylaminobenzamidine hydrochloride. The insoluble residue was crystallised repeatedly from alcohol and obtained in pure white needles melting at 238° (246° corr.). The substance contained no chlorine and formed no salts. (Found: C=73·46; H=6·04· N=13·3. $C_{13}H_{12}ON_2$ requires C=73·6; H=5·7; N=13·2 per cent.) The solubility and general relations indicated *s*-diphenylcarbamide.

An interesting point noticed was that for some weeks after the reaction in the mixture had been proceeding, the separated substance contained scarcely any diphenylaminobenzamidine salt, but consisted almost entirely of the carbamide. After several months, however, the separated solid contained little of the carbamide and consisted mostly of the salt, showing that the latter forms only slowly. The formation of diphenylcarbamide is interesting; probably a dichloro-compound, $CCl_2(NHPh)_2$, is formed first, which is then hydrolysed by water, either present originally in the mixture or entering subsequently from the air. That the water was present at the beginning is indicated by the gradual falling off in the production of the substance as the experiment was prolonged.

Mixture 4.—This was a mixture containing a very large excess of carbon tetrachloride; it consisted of the first fraction in the separation of carbon tetrachloride and aniline by fractional distillation, to which a small amount of aniline had been added. On keeping in a closed bottle, it gradually became brown, and, after two months, deposited a mass of crystals, some having a deep blue colour. No catalyst was added.

The separated substance proved to be a complex mixture of several different compounds. After many trials, the following scheme of separation was adopted: The whole mass, weighing about 5 grams, was extracted repeatedly with light petroleum in a Soxhlet apparatus for several hours. The brown extract gave on evaporation a few milligrams of dark solid which, when crystallised from carbon tetrachloride, appeared in very small, reddish-brown prisms melting at 237° (245° corr.). It was insoluble in water, dilute acids, or alkalis, and could not be identified. The substance in the Soxhlet tube was extracted repeately with ether, leaving behind a dark blue residue. The ethereal extract was found to contain diphenylcarbamide, which was separated and purified. The blue residue contained at least two substances, and many solvents were tried without any success in separating them. This was finally accomplished by fractional sublimation under diminished pressure. Much aniline hydrochloride sublimed, leaving a few milligrams of dark blue solid behind.

The blue substance contained carbon, hydrogen, nitrogen, and chlorine; it dissolved in water, alcohols, and other solvents, giving deep blue solutions. With sodium hydroxide, it gave a pink solution, the colour rapidly disappearing on boiling. This would indicate possibly a basic dye. Direct dyeings on silk, wool, and cotton were made. On silk, the colour was a deep purple blue, scarcely affected by exposure to sunlight or by washing in weak acids or alkalis. On wool, the dyeings were deep grey blues, fast

to light, and resisted boiling in soapy water fairly well. The results on cotton were poor, even with mordants. Attempts to identify the dye were not successful, and no investigation of the constitution could be undertaken on account of the very small amount available.

A small quantity of azobenzene was obtained from the mother liquors of Mixture 4 after removal of the crystals which had formed.

The results of the investigation may be summarised as follows: Previous observations by Hofmann and others have shown that carbon tetrachloride and aniline react slowly together at 180° giving diphenylaminobenzamidine and pararosaniline. It is now found that this action takes place very slowly at the ordinary temperature, the products varying with the original mixture and the conditions. Neglecting the brown discolorations soon appearing, the first product, after some weeks' action, seems to be *s*-diphenylcarbamide, produced by the hydrolysis of a dichloro-substitution product of carbon tetrachloride by small amounts of water present in the reaction mixture. The formation of diphenylaminobenzamidine is a slower process and takes some months. In solutions of certain composition, small quantities of coloured products may be obtained, the formation of which is probably indirect. Two such products have been isolated in the pure state, one in minute brown crystals and the other as a deep blue substance with dyeing properties.

In the presence of a copper–mercury couple, the reaction is comparatively rapid. At the ordinary temperature, a small amount of pararosaniline is formed, as well as phenylcarbylamine and a fair amount of azobenzene. The main product is, however, diphenylaminobenzamidine hydrochloride. At 80—90°, the reaction is rapid, the product consisting of the diphenylaminobenzamidine salt with some small amount of pararosaniline. In all cases, however, the reaction is not completed, and only the main constituents of the very complex mixtures have been identified. It would appear from the results of Hofmann and Weith as to the formation of pararosaniline that the yield of this substance is favoured by increasing the temperature, it possibly being formed by intramolecular rearrangement from the isomeric diphenylaminobenzamidine. Some experiments were made to convert this base into the dye by raising the temperature in the presence of various substances, but without success.

The use of the copper–mercury couple makes the preparation of diphenylaminobenzamidine from aniline and carbon tetrachloride a simple matter, and a fair yield is obtained. Further, as both

aniline and carbon tetrachloride are characteristically type substances, the range of action of this catalyst will probably be extensive in reactions between related compounds.

My sincere thanks are here expressed to Professor Orme Masson for his continued interest in, and kindly criticism of, this work.

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[*Received, October 1st, 1917.*]

XX.—*The Synthesis of Ammonia at High Temperatures.*

By EDWARD BRADFORD MAXTED.

IF the equilibrium between nitrogen, hydrogen, and ammonia be examined thermodynamically, it will be seen that whereas at moderate temperatures, such as are employed for the catalytic synthesis of ammonia, an increase in temperature leads to a rapid decrease in the amount of ammonia in equilibrium with nitrogen and hydrogen, this amount passes at higher temperatures through a minimum and, with increasing temperature, begins to rise with increasing velocity.

For a rough preliminary calculation, either of the following formulæ, which have been worked out by Haber (*Zeitsch. Elektrochem.*, 1914, **20**, 597; "Thermodynamics of Technical Gas Reactions," p. 204) for the ammonia equilibrium at temperatures below 1000°, may be extended to higher temperatures in order to demonstrate this reversal, but it will be shown that more ammonia is actually obtained at, for instance, the temperature of the oxyhydrogen flame than can be accounted for by either formula.

We have, accordingly, if $K = \dfrac{P_{NH_3}}{P^{\frac{1}{2}}_{N_2} \times P^{\frac{3}{2}}_{H_2}}$:

(*a*) $\log_{10}K_p = 2215/T - 3{\cdot}625 \log_{10}T + 0{\cdot}000307T + 0{\cdot}29 \times 10^{-6}T^2 + 4{\cdot}82$.

(*b*) $\log_{10}K_p = 2098/T - 2{\cdot}5088 \log_{10}T - 0{\cdot}0001006T + 0{\cdot}186 \times 10^{-6}T^2 + 2{\cdot}1$.

The calculated variation of K with temperature is given in the following table.

TABLE I.

Temperature.	Value of $K \times 10^4$. By equation (a).	By equation (b).
1000° Abs.	5·7	5·7
2000	0·78	0·26
3000	3·03	0·28
4000	152·0	1·5

It was accordingly to be assumed that mixtures of nitrogen and hydrogen, at high temperatures, contain ammonia which by rapid cooling might be brought, without complete decomposition through the temperature zone at which ammonia becomes unstable into that region of temperature in which it is once more capable of stable existence.

The subject has been examined experimentally, first for not extremely high temperatures, by rapidly cooling mixtures of nitrogen and hydrogen from the temperature of the oxy-hydrogen flame to the ordinary temperature, yields of ammonia amounting to more than 1 per cent. by volume under atmospheric pressure being obtained. The result is of special interest if one considers that such a yield is only possible otherwise below 350°, a temperature at which the formation of ammonia, even in the presence of catalysts, does not proceed with measurable velocity.

The method of heating and suddenly cooling employed in the work about to be described consists in injecting the mixture of nitrogen and hydrogen into an oxy-hydrogen flame burning under water, or, in a second series of experiments, into an oxy-hydrogen flame burning in a water-cooled silica tube, the amount of ammonia formed being estimated in some cases by direct titration with $N/10$-acid and in others colorimetrically by Nessler's solution. The reaction mixture contained, therefore, in addition to nitrogen and hydrogen, a volume of steam depending on the proportion of the mixture of nitrogen and hydrogen injected into the flame. It was noted, further, that the yield of ammonia recovered at the ordinary temperature was considerably greater when direct cooling with water was employed than when the flame was cooled by contact with a water-cooled quartz tube.

EXPERIMENTAL.

For the first series of experiments, the reaction chamber consisted of a silica tube 6·5 mm. in diameter and 7·5 cm. long, completely immersed in about 900 c.c. of distilled water contained in a glass vessel fitted with an efficient glass cooling coil through which

a rapid current of water was passed, the vessel having a capacity of slightly more than 1 litre. Into the quartz reaction chamber, nitrogen, hydrogen, and oxygen, at rates determined by velocity meters, were injected and ignited, the flame gases passing out of the open end of the reaction chamber and bubbling through the water, by the action of which the ammonia, recovered from the flame by sudden cooling, was retained. In some cases the water was replaced by dilute acid, without, however, any appreciable difference in the results, provided that the water was kept cool. The amount of oxygen passed into the reaction chamber was in every case regulated in such a way as to leave uncombined hydrogen equal to three times the volume of the nitrogen passed in.

In order to make a comparison of the results obtained at various temperatures and at varying partial pressures, that is, by the increasing dilution of the oxy-hydrogen flame with a mixture of nitrogen and hydrogen, advantage was taken of the known fact that for small percentages of ammonia the volume formed at a given temperature is directly proportional to the pressure, so that the volume of ammonia which would be formed at the temperature of the flame but under atmospheric pressure may be calculated by dividing the value observed by the corresponding partial pressure of the nitrogen, hydrogen, and ammonia in the nitrogen, hydrogen, ammonia, and steam reaction mixture. In this way, it becomes possible easily to compare the relative amounts of ammonia formed at different temperatures and under varying partial pressures. In this series of experiments, the ammonia in the resulting solution was estimated colorimetrically by Nessler's reagent, care being taken to use distilled water free from ammonia for cooling the flame. In those cases in which dilute acid was used for cooling, this was made up by dissolving 40 c.c. of ammonia-free $N/10$-sulphuric acid in each litre of distilled water.

Table II summarises the results obtained by direct cooling with water or dilute acid.

It will be noticed that the percentage of ammonia by volume in the mixture of nitrogen and hydrogen recovered by suddenly cooling (reduced for uniformity to one atmosphere pressure) rises from 0·0027 to 1·23 as the reaction temperature approaches that of the oxy-hydrogen flame. The flame temperatures are calculated from Féry's observed values for the oxy-hydrogen and air-hydrogen flames.

Experiments with Indirect Cooling.

The reaction chamber employed for this series of experiments consisted of a vertical quartz tube 90 cm. long and 8 mm. in

TABLE II.

No. of expt.	Velocity in litres per hour of gases passed into reaction chamber.			Duration of expt. in minutes.	Cooling agent.	Percentage by volume of ammonia in mixture of nitrogen and hydrogen.	Partial pressure of system nitrogen–hydrogen–ammonia in flame.	Estimated temperature of flame. ° Abs.	Percentage volume of ammonia formed at absolute pressure of 1 atm.
	Nitrogen.	Hydrogen.	Oxygen.						
1	60	220	20	15	Acid	0·00235	0·86	1280	0·0027
2	60	260	40	15	Water	0·005	0·75	1500	0·0067
3	60	360	90	15	Water	0·013	0·57	1830	0·023
4	30	270	90	15	Water	0·018	0·4	2120	0·045
5	20	240	90	15	Water	0·0205	0·31	2260	0·066
6	20	300	120	10	Acid	0·0366	0·25	2350	0·146
7	20	460	200	5	Acid	0·07	0·167	2470	0·42
8	10	430	200	5	Acid	0·112	0·091	2580	1·23

internal diameter. This was cooled by making it the inside tube of a long Liebig's condenser. The flame gases, which in this case were cooled only by contact with the cold walls of the silica tube, were allowed to pass from the bottom of the tube through a known quantity of $N/10$-acid, which was afterwards titrated with alkali in the usual manner. As was to be expected from the less rapid cooling, the amount of ammonia produced at high temperatures was less than that obtained by directly leading the flame into cold water. At lower temperatures, the divergence became less marked until, at the lowest temperature studied, approximately equal values for the yield of ammonia were observed. The results obtained by indirect cooling in the above manner are summarised in table III.

TABLE III.

No. of expt.	Duration in minutes.	Partial pressure of system nitrogen–hydrogen–ammonia in flame.	Percentage by volume of ammonia in mixture of nitrogen and hydrogen.	Estimated temperature of flame. ° Abs.	Percentage volume of ammonia at absolute pressure of 1 atm.
1	30	0·86	0·0026	1280	0·003
2	30	0·57	0·0068	1830	0·012
3	30	0·25	0·0134	2350	0·054
4	30	0·167	0·0196	2470	0·118
5	30	0·091	0·019	2580	0·21

Summary.

It may be shown thermodynamically that the ammonia equilibrium first sinks with increasing temperature, then passes through a minimum, and finally rises again. By suddenly cooling mixtures of nitrogen and hydrogen, much of the ammonia contained therein may be obtained at the ordinary temperature, and the ammonia formed is, if we assume Féry's measurements for the temperature of the oxy-hydrogen flame to be correct, greater than corresponds with Haber's equation for the ammonia equilibrium at temperatures below 1000°. With direct cooling of flames by means of water, volumes of ammonia amounting for atmospheric pressure to 1·23 per cent. of the mixture of nitrogen and hydrogen have been obtained. With indirect cooling, less ammonia is recovered, the maximum volume per cent. obtained at atmospheric pressure being 0·21.

GAS DEVELOPMENTS, LTD.,
WALSALL.

[*Received, December 29th*, 1917.]

XXI.—*A Reinvestigation of the Cellulose-Dextrose Relationship.*

By Mary Cunningham.

It has been assumed that in order to determine the structure of the cellulose molecule, an obvious course is to identify quantitatively the products of ultimate hydrolysis and from their known constitution to reconstruct the original complex. Hence the commonly accepted view of (cotton) cellulose as a polydextrose anhydride. Recent researches have, however, cast doubt on such interpretation of the results of hydrolytic resolution, for they have shown that a molecular structure is not necessarily that of its constituents after hydrolysis (Fischer, *Ber.*, 1914, **47**, 1980; Irvine, Fyfe, and Hogg, T., 1915, **107**, 524; Haworth and Law. T., 1916, **109**, 1314). Moreover, and particularly as regards cellulose, observations of optical activity and reducing power of the products of resolution have been accepted as unquestionable evidence of identification, whilst the isolation of the substances having the recorded constants has even been regarded as superfluous. It seemed important, therefore, on this basis of criticism to reinvestigate the products formed from cellulose by the action of acids which have usually been regarded as giving maximum resolution, namely, sulphuric acid dihydrate, $H_2SO_4,2H_2O$, and hydrochloric acid of more than 40 per cent. concentration.

Two classes of cellulose have been selected for experiment, namely, cotton cellulose as the normal type, and esparto cellulose, which is characterised by a high furfuroid content, resembling in this respect the cereal celluloses, but being more resistant to hydrolysis. In the case of cotton cellulose, particular attention has been paid to the action of 40 per cent. hydrochloric acid, as the behaviour of the normal cellulose to sulphuric acid has already been studied by numerous investigators (compare Flechsig, *Zeitsch. physiol. Chem.*, 1883, **7**, 523; Stern, T., 1895, **67**, 74; and Ost and Wilkening, *Chem. Zeit.*, 1910, **34**, 461). Esparto cellulose has not, however, previously been examined in this respect, but it has now been found that treatment with 73 per cent. sulphuric acid results in the formation of polysaccharose esters, which were usually obtained as barium salts. These compounds bear sufficient relation to the original complex to give a high, although diminished, yield of furfuraldehyde on distillation, but they are distinguished from the cotton cellulose sulphates prepared by Stern (*loc. cit.*), by the action of concentrated sulphuric acid, in having a much smaller

content of inorganic material. In the esparto products, the proportion of barium combined is approximately equal to that of SO_4, so that the two are present in the ratio $Ba_2:(SO_4)_3$. This means that if either neutral or acid sulphates or both are formed with alcoholic hydroxyl groups, then an excess of barium is present which must be in union with hydroxyl groups of a sufficiently acid character to decompose barium carbonate, whilst the acid character of these hydroxyl groups is further emphasised by the stability of the compounds towards carbon dioxide, and this establishes them as genuine barium salts. The SO_4 residues are also in very stable union, as complete precipitation can only be effected by boiling with concentrated hydrochloric acid in the presence of barium chloride for some hours, and although alkaline hydrolysis with barium hydroxide solution greatly increases the barium content, the SO_4 groups are not entirely removed, and it is quite possible that some of them are present in the form of a neutral ester.

As regards hydrolysis by the action of 40 per cent. hydrochloric acid, the claim has been put forward that cotton cellulose under these conditions is quantitatively resolved into dextrose. It must be remembered, however, that this conclusion and the theoretical considerations to which it obviously leads were based, not on the yield of dextrose actually isolated, but, by inference, on the specific rotation and reducing power of a 1 per cent. solution of cellulose in the acid,* the yield of dextrose being calculated from the formula $c = \alpha \times 100/[\alpha]_D$, where $[\alpha]_D$ is the specific rotation of dextrose in 40 per cent. hydrochloric acid (Willstätter and Zechmeister, *Ber.*,

* Willstätter and Zechmeister appear to have overlooked the elaborate investigation of J. König, and F. Hühn, "Bestimmung der Zellulose" (Berlin, 1912). In investigating celluloses isolated by the several hitherto recognised standard methods (Hugo Müller, Cross and Bevan, König, Tollens, Schulze, etc.) they employ the method of solution in the zinc chloride–hydrochloric acid reagent (Cross and Bevan) and polarimetric observations of the solutions. In this reagent, dextrose was found to have a maximum $\alpha_D + 60°$ and xylose $+32°$.

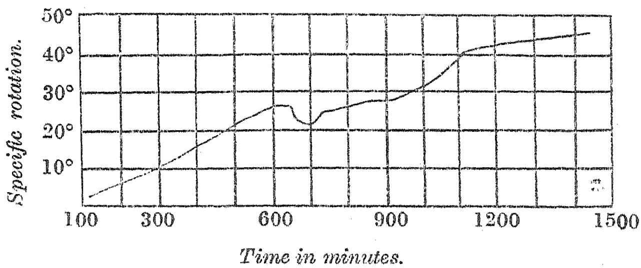
Comparing these solutions of the celluloses (derivatives) there is a maximum for α_D of $+82.5°$ in the case of cotton cellulose "purified" by the König method; the maxima are very variable over the special range of products investigated.

These authors do not draw the conclusion that dextrose is formed as such, or that the rotations, although apparently specific, are attributable to ultimate groups, namely, hexose (or pentose). What they state is that maximum of rotation is a criterion of maximum "purity" of cellulose. This conclusion has been examined in a communication dealing critically with the whole paper (Cross and Bevan: *Eighth Int. Congr. App. Chem.*, 1912, **13**, 101). No doubt attaches to their experimental numbers and, being directly relevant to the issue raised by Willstätter and Zechmeister, they have to be taken into consideration.

1913, **46**, 2401). Such data seemed entirely inadequate in view of the fundamental character of the issues involved, and it was therefore decided to repeat the polarimetric observations * and also to isolate the products in solution after definite intervals of

FIG. 1.

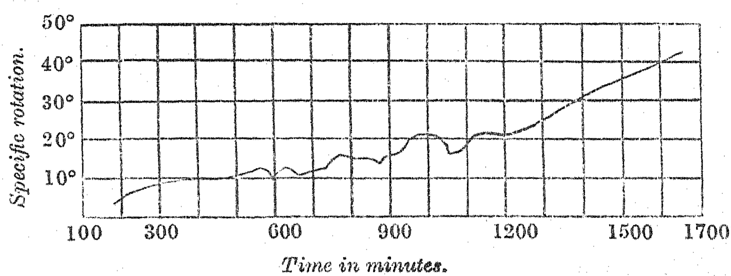
Hydrolysis of cotton cellulose with 40 per cent. hydrochloric acid.



time. The changes in optical activity were observed as nearly as possible every 30 minutes for 24 hours, and the results are shown graphically in Figs. 1 and 2. It will be observed from Fig. 1 (cotton cellulose) that there is a continuous increase in

FIG. 2.

Hydrolysis of esparto cellulose with 40 per cent. hydrochloric acid.



activity up to 600 minutes, but then a marked fall occurs, followed by a fairly regular rise to the value $[\alpha]_D$ +45·6° at the end of 1400 minutes, with a further increase of 10° during the next 13 hours.

* The polarimetric observations were made after dilution, owing to the doubtful condition of sugars when dissolved in strong acids. Mutarotation to the α-form assumed by Willstätter is not a satisfactory explanation of the remarkable increase in activity observed, for dextrose shows in acid containing 44·5 per cent. of hydrogen chloride a specific rotation 60° above that of the α-isomeride, and this suggests more profound constitutional change than merely isomeric transformation.

Esparto cellulose (Fig. 2) showed for the most part similar fluctuations in rotation, but the initial attack of the acid is less delayed, whilst more irregularities occur in the middle portion of the curve, and the final value for the specific rotation is somewhat lower. The hydrolytic solutions were diluted and neutralised at the end of 24 hours, when the esparto solution gave $[\alpha]_D +41{\cdot}1°$ and the cotton cellulose solution $45{\cdot}6°$, but in the latter case a separation of the products was also made at the end of 48 hours, since the specific rotation had risen to the value $56{\cdot}5°$, which is very nearly that of dextrose calculated according to the equation

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

The substances so prepared were lead salts of polysaccharose esters similar to the barium salts previously described, the higher molecular proportion of chlorine entering into combination according with the superior esterifying power of hydrochloric acid as compared with sulphuric acid. Dextrose could not be identified in any of the fractions, and, if present, it would appear and be concentrated in the more readily soluble portions, but these show a higher inorganic content and a lower specific rotation. The possibly misleading character of polarimetric observations when unsupported by the full identification of products is also emphasised by the fact that whilst solutions of the very divergent types of cellulose investigated show almost concordant optical activity, the esparto products are furfuroids, and their solution gives, throughout the hydrolysis, high yields of furfuraldehyde with a final loss of only 3 per cent., even if neutralisation is postponed for six days. Further, dextrose is not formed on subsequently heating the salts with dilute acid. Both the sulphates and the chlorides so treated show a fall in optical activity, whilst the products, isolated after the rotation has become constant, contain a diminished quantity of inorganic material, and, in the case of esparto, give a smaller yield of furfuraldehyde on distillation. Evidently, therefore, the main action of the acid is to cause further condensation of the original complex, and not hydrolysis to sugar. The same is even true of a sulphate prepared free from barium by the action of cold sulphuric acid on an alcoholic solution of the salt. It should be mentioned, however, that by the sulphuric acid hydrolysis of the barium salts, residual syrups are obtained which give glucosazones in small yield. The ester salts are further characterised by a marked reducing power and also by showing slight mutarotation which is uniformly downwards. These observations indicate that the compounds are correctly described as ester salts of polysaccharoses, and it is possible that they represent the initial results

of hydrolysis and are not "reversion products" (Ost and Wilkening, *loc. cit.*), as otherwise the fluctuations in optical activity would have been more marked. On the other hand, the main result of these experiments, that no quantitative resolution of cellulose to dextrose is in reality obtainable, reopens the whole question of the structure of the complex. This aspect of the matter is, however, dealt with in the following paper by Messrs. Cross and Bevan.

EXPERIMENTAL.

The Action of Sulphuric Acid Dihydrate, $H_2SO_4,2H_2O$, *on Esparto Cellulose.*—Sixty grams of cellulose, dried at 80°, were mixed with 300 c.c. of 73 per cent. sulphuric acid in a stoppered bottle. The bottle was mechanically shaken for six hours, and the very viscous solution allowed to remain for a further 18 hours, when it was diluted with 2 litres of water. A very small amount of regenerated cellulose was obtained, and the excess of sulphuric acid was removed by the addition of barium carbonate, followed by filtration. The syrup left after concentration of the filtrate was dissolved in 50 per cent. alcohol, and from this solution, after filtering, 37 grams of a white, amorphous product were obtained by the addition of 80 per cent. alcohol, whilst 8 grams of a second fraction were precipitated from the filtrate by means of absolute alcohol. Both fractions were very deliquescent and were only prepared in a solid form with difficulty. Drying operations had to be carried out at 50—60°, as charring easily took place, and the excessive swelling which accompanied it rendered elementary analysis impossible.

Fraction I.—Found: Ba = 8·6; SO_4 = 7·9; $C_5H_4O_2$ (furfuraldehyde) = 8·3. $[\alpha]_D$ +47·8° to 45·5°.

Fraction II.—Found: Ba = 8·6; SO_4 = 10·6; $C_5H_4O_2$ = 8·0 per cent. $[\alpha]_D$ +55·3° to 51·6°.

Preparation of an Ester Free from Barium.—In attempting to isolate an ester free from barium, it was desired to avoid any further hydrolysis of the original product, and therefore the barium salt remained in acid alcoholic solution for some days in the cold. Barium sulphate was then removed by filtration, and the addition of absolute alcohol to the filtrate gave a white, amorphous precipitate entirely free from ash.

Found: SO_4 = 5·3; $C_5H_4O_2$ = 6·2 per cent. $[\alpha]_D$ +41·6°.

Hydrolysis of Barium Salt with 2 per cent. Sulphuric Acid.—An 8·5 per cent. solution of the barium salt was made up in 2·3

per cent. sulphuric acid, and the following changes in optical activity were observed:

Initial specific rotation		42·3°
After heating at 100° for	20 minutes	34·5
,, ,, ,, ,,	40 ,,	32·8
,, ,, ,, ,,	100 ,,	30·8 (constant)

At this stage in the hydrolysis, the acid solution was neutralised with barium carbonate, and after concentrating the filtrate, the syrupy residue was dissolved in 50 per cent. alcohol, and the solution gave a white, amorphous precipitate on the addition of absolute alcohol. The yield only amounted to 60 per cent.

Found: Ba = 5·3; SO_4 = 6·0; $C_5H_4O_2$ = 5·0 per cent. $[\alpha]_D$ +33·8°.

Hydrolysis of Barium Salt with 5 per cent. Barium Hydroxide Solution.—The barium salt was heated at 100° with the alkali for 7 hours. An immediate precipitation of barium sulphate occurred, but the resulting compound, isolated as usual, still contained a small percentage of SO_4. The barium content was greatly increased, and this probably indicates the presence of hydroxyl groups in the original complex, sufficiently acidic to combine with barium, but not able to decompose barium carbonate. The compound was too dark for polarimetric observations.

Found: Ba=25·1. SO_4=2·4 per cent.

The Action of 40 per cent. Hydrochloric Acid on Cotton Cellulose. (a) *Changes in Optical Activity.*—A 5 per cent. solution of cotton cellulose in 40 per cent. hydrochloric acid was prepared, and the polarimetric readings were taken after the concentration had been lowered to 1 per cent. This gives an acid concentration of 8 per cent., in which, as shown by Willstätter, the specific rotation of dextrose is practically normal. The readings at 15°, from which the foregoing curve was constructed (Fig. 1), are given below.

Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.
120	3·2°	385	14·8°	635	26·0°	900	28·4°	1245	42·4°
150	3·2	415	16·4	675	22·4	930	29·2	1290	44·0
180	5·6	455	19·2	705	22·4	1010	32·8	1330	44·8
210	6·0	485	20·0	735	25·2	1040	34·8	1375	44·8
240	8·0	515	21·6	765	24·8	1070	37·6	1400	45·6
295	10·4	545	22·4	795	26·4	1100	39·2	1435	45·6
325	11·2	575	24·2	825	27·6	1160	40·8	2250	56·8
355	12·8	605	26·0	870	28·0	1195	41·6		

It will be seen that, except for some irregularities in the period 635 to 825 minutes, the optical activity continuously increases to the final value +56·8° at the end of 2250 minutes. The values for $[\alpha]_D$ are calculated on the original weight of cellulose.

(b) *Yield of Furfuraldehyde.*—At the end of 24 hours, the acid solution was diluted to 12 per cent. and distilled, as in the ordinary procedure for a furfuraldehyde estimation. The yield only amounted to 1·2 per cent., calculated on the original weight of cellulose, so that evidently the high furfuroid content of the esparto solution is due to the persistence of the original complex and not to any specific action of the acid treatment.

(c) *Isolation of the Products formed after Hydrolysis for* (1) 24 *Hours*, (2) 48 *Hours.*—When the specific rotation had reached the value +45·6° at the end of 24 hours, the acid solution was diluted to 1 litre and neutralised with lead carbonate. The filtrate was then concentrated under diminished pressure, and the syrupy residue freed from any lead chloride retained as impurity by precipitation with hydrogen sulphide and subsequent neutralisation with silver carbonate. Some lead sulphide was formed, but very little acidity developed, and it is therefore possible that a portion of the precipitated lead was in combination with an organic compound. After further concentration in a vacuum, a clear, colourless syrup was obtained which dissolved readily in 80 per cent. alcohol, and the addition of absolute alcohol precipitated from it 2·5 grams of a white, amorphous, deliquescent compound. A second fraction was obtained from the filtrate amounting to 3·1 grams, and there then remained 1·3 grams of residual syrup, which also contained lead and chlorine. The total yield of products is therefore only 69 per cent.

Fraction I.—Found: Pb = 7·9; Cl = 6·1; $C_5H_4O_2$ = 1·08. $[\alpha]_D$ +48·2° to 43·0°.

Fraction II.—Found: Pb=8·2; Cl=7·3 per cent. $[\alpha]_D$ +46·7° to 33·4°.

(2) *Products Formed after 48 Hours' Hydrolysis.*—The products in solution after the more prolonged hydrolysis were separated as previously described, but their general characteristics were quite similar, although the specific rotation of the acid solution had increased to the constant value +56·8°. The yields from 10 grams of cellulose were: fraction I, 2·1 grams; fraction II, 3·9 grams with 0·9 gram of residual syrup, also containing lead and chlorine.

Fraction I.—Found: Pb=8·3; Cl=6·2. $[\alpha]_D$ +42·5° to 34·5°.

Fraction II.—Found: Pb=9·4; Cl=9·8 per cent. $[\alpha]_D$ +26·7° to 17·3°.

The Action of 40 *per cent. Hydrochloric Acid on Esparto Cellulose.* (a) *Changes in Optical Activity.*—A 5 per cent. solution of esparto cellulose was prepared as previously described in the case of cotton cellulose. The esparto solution darkened more quickly

and the precipitated cellulose was more discoloured. The darkening of the solution was due to the separation of humus substances which were not entirely soluble in alkali. The polarimetric observations were taken as before, at 15°, after dilution to 1 per cent. concentration, reckoned on the original weight of cellulose.

Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.	Minutes.	$[\alpha]_D$.
130	8·4°	460	22·4°	750	30·4°	990	35·0	1330°	39·2°
155	9·2	490	24·8	780	29·6	1030	34·4	1405	40·0
185	9·6	535	26·8	810	29·6	1075	37·6	1490	41·1
215	10·8	570	27·2	840	30·4	1135	39·2	1620	46·3
245	11·6	600	28·4	870	32·0	1165	38·4	1770	45·6
290	13·6	630	29·2	900	31·2	1200	40·0	2035	46·3
320	15·2	670	31·2	930	35·1	1230	38·4	2250	46·3
370	18·0	735	32·4	960	35·0	1295	39·2	3000	54·4
400	19·6								

It will be seen that for the most part the changes in optical activity are parallel to those recorded in the case of cotton cellulose.

(b) *Variations in Yield of Formaldehyde.*—The yield of furfuraldehyde was determined at definite intervals by distilling a portion of the acid solution after the acid concentration had been reduced to 12 per cent.

Time from start.	$[\alpha]_D$.	Yield of furfuraldehyde, per cent.
12 hours	29·5°	11·6
24 ,, ...	41·4	11·6
6 days	49·6	9·9

The yield of furfuraldehyde is calculated on the original weight of cellulose dissolved.

(c) *Isolation of the Products of Hydrolysis.*—At the end of 24 hours, the acid solution was treated as described under cotton cellulose. The products contained a complex which yielded furfuraldehyde, but otherwise they had the same general characteristics. As usual, drying operations had to be conducted with great care, as charring easily occurred, accompanied by marked swelling, which rendered an elementary analysis impossible.

Fraction I.—Found: Pb = 7·9; Cl = 5·6. $[\alpha]_D$ + 30·5° to 22·2°.

Fraction II.—Found: Pb = 8·2; Cl = 8·6; $C_5H_4O_2$ = 5·7 per cent. $[\alpha]_D$ + 32·2° to 25·2°.

The total yield was only 40 per cent. of the weight of cellulose employed.

Summary and Conclusions.

(1) The products of hydrolysis of the celluloses are not identifiable by the rotation constants of the hydrolytic solutions. The latest conclusions as to the cellulose–dextrose relation, based on

optical data, are now shown to be invalidated, for the following reasons: (*a*) Such widely different types as cotton and esparto celluloses give identical optical data on hydrolysis, but the ultimate products have necessarily divergent constitutions. (*b*) Solution in concentrated hydrochloric acid produces constitutional changes even in the simple hexoses of known configuration, as shown by the marked fluctuations in optical activity accompanying slight variations in acid concentration. The products obtained in acid solution from cellulose may therefore be the result of several concurrent reactions. Even when these are reduced to a minimum by sufficient dilution, there is still the ascertained complication of esterification.

(2) No quantitative resolution of cellulose to dextrose has yet been obtained, and the claim made by Willstätter and Zechmeister to have effected this conversion, since it rested solely on polarimetric observations and the equally non-specific data of cupric reduction, would seem inadmissible.

(3) Isolation and identification of the products of hydrolysis or their immediate and characteristic derivatives must be regarded as the only trustworthy means of quantitatively studying the resolution of highly complex colloidal carbohydrates such as cellulose.

(4) Under the action of both sulphuric and hydrochloric acids, cellulose forms esters of polysaccharoses which contain acidic hydroxyl groups. In the case of hydrolysis by the latter acid especially, attempts to isolate dextrose, if present, by fractionation only resulted in the production of compounds having a higher content of inorganic material and a lower specific rotation, whilst the effect of subsequent heating with dilute acid is to produce, not hydrolysis, but further condensation.

I wish to express my indebtedness to the Carnegie Trustees, who provided the opportunity for carrying out this research, also to Professor J. C. Irvine and Mr. C. F. Cross, who have given me valuable advice, and, lastly, to Messrs. Tullis, Russell and Company, who kindly supplied the esparto products used in the experiments.

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XXII.—*Esparto Cellulose and the Problems of Constitution.*

By CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN.

THE study of cellulose by way of processes of "solution" and of its ester derivatives through their solutions has extended rather than deepened our knowledge of cellulose matter; for progress in the more fundamental regions there are required (*a*) a comprehensive study of physical constants and (*b*) an exhaustive study of processes and products of resolution. We have devised a plan of investigation towards these ends, and in the former (*a*) we are joined by S. S. Napper and S. J. Lewis; Dr. Lewis has made substantial progress in measuring fluorescence effects, absorption spectra, diathermancy, but more especially density-volume phenomena, the results of which promise to throw light on fundamental points. These researches will be the subject of future communications.

The latter (*b*) specially sets out from a critical survey of the evidence for the generally accepted view of cellulose as a polyhexose anhydride, that is, with ultimate groups of configuration conforming closely with that of dextrose. In this critical study and in the resulting scheme of experimental revision of the accepted evidence—based on resolutions assumed to be purely hydrolytic—we are joined by Professor J. C. Irvine, in whose laboratory the work described by Miss Cunningham in the preceding paper has been carried out.

The selection of esparto cellulose as a type for parallel study with the normal cotton cellulose is justified by considerations a priori and by the results of our own further study of this product undertaken concurrently.

(1) Esparto cellulose presents striking divergences from the other celluloses in the well-established characteristics (*a*) of reactivity with aniline—the rose-red colour reaction is sufficiently constant to be a measure of the proportion of esparto cellulose in admixture with cotton and wood celluloses, and (*b*) of yielding a constant high proportion of furfuraldehyde (12·5 per cent.) when decomposed with acids by the usual methods.

These are an index and measure of constitutional features of differentiation both of proximate and ultimate groups.

(2) Esparto cellulose is grouped with the cereal celluloses which present these same specific characteristics; but the latter are complex mixtures of structural elements, whereas esparto cellulose, as

paper-maker's "pulp," is a substantially homogeneous type—an assemblage of the fusiform, elongated cells which are identified as preponderating in the leaf structure by examination of transverse sections. It should be noted that the cereal celluloses are derived from stem tissues (straw), and the structural differentiation corresponds with difference of function.

(3) The cereal celluloses, as regards ultimate composition, are differentiated from the normal (cotton) celluloses by containing a lower percentage of carbon.

With Mr. Napper we have carefully purified specimens of esparto cellulose, and he has obtained the following analytical numbers with a specimen which, when dried at 100° in dry nitrogen, lost 'moisture' = 7·2 per cent., and on burning left 0·2 per cent. of ash:

0·1808 gave 0·2962 CO_2 and 0·0995 H_2O. C = 44·68; H = 6·16 per cent.*

These figures are approximately those required for the normal substance, and since the "furfuroid" constituent groups must be inferred from the yield of furfuraldehyde (12·5 per cent. as determined on the specimen in question) to be approximately 30 per cent. of the (esparto) cellulose aggregate, it would appear that the two component celluloses are identical in elementary composition. This does not allow any positive conclusions as to the generally assumed identity of 'furfuraldehyde-yielding' with pentosan groups. As, however, the full anhydride, of empirical formula $C_5H_8O_4$, requires C = 45·5 per cent., the evidence on this point, taken together with experimental facts set forth below, is rather against this assumption.

(4) It is noteworthy that as a result of the reaction with concentrated aqueous hydrochloric acid, as described in the foregoing paper, there is a loss of total furfuraldehyde, that is, a disappearance of "furfuroid" groups as such. This constitutional change has been studied and more definitely established by means of reactions calculated to determine the minimum of change in groups of normal hexose- or pentose-configuration.

These results are briefly as follows.

Action of Alkali Hydroxide.

(a) *Sodium Hydroxide* (4 *per cent.*) *at* 135°.—We must premise that esparto cellulose is isolated by digesting the raw esparto with 17 per cent. of its weight of 3—4 per cent. sodium hydroxide solution at 130° and under the corresponding pressure. It survives

* Calc. to (dry) ash-free substance.

this treatment with no change of furfuroid contents. Moreover, from the liquor we have isolated a colloidal or 'pectic' furfuroid, giving 50 per cent. of furfuraldehyde on boiling with hydrochloric acid. This is a higher yield than from any compound of this class hitherto obtained, and would appear to characterise it as a 'pure' pentosan. It is mentioned here only in reference to one point, namely, its behaviour with the hydrolysing acid employed in resolving the esparto cellulose (*infra*). The fuller study of this interesting substance is incidental to our scheme of research, which embodies the systematic fractionation and characterisation of these by-products of the industrial process, and the extension of our previous investigations (T., 1882, **41**, 94). The results of these researches will form the subject of future communications.

(b) *Sodium Hydroxide* (17·5 *per cent.*) *at* 15—20°.—Treatment with 'mercerising soda' is a standard method of diagnosing the proximate constitution of industrially important celluloses. The following numbers were obtained with the specimen in question, that is, the product from (*a*) subsequently purified by the usual basic bleaching process (bleaching powder):

α-Cellulose (resisting the solvent action)	84·14
β-Cellulose (soluble and reprecipitated on acidification)...	—
γ-Cellulose (hydrolysed: soluble in acidified liquid).........	15·86

[The specimen contained 1·3 per cent. of mineral constituents (ash), and the above figures are calculated on the ash-free cellulose.]

Action on Furfuroid Complex and Furfuroid Groups.

The yields of furfuraldehyde were:

Original cellulose. Per cent.	Cellulose after treatment.
	α-Cellulose 84·14 : 4 per cent. = 3·36
	γ-Cellulose 15·86 : 26 ,, = 4·12
12·5	Total per cent. .... 7·48

There is an important constitutional change determined by the mercerisation: 40 per cent. of the ultimate furfuroid groups are affected, and the change of structure is more pronounced in the resistant (α) complex than in the hydrolysed groups (γ).

Action of Acids.

(a) *Acetylation.*—The cellulose was acetylated, with a yield of 160 per cent. of the weight taken. The acetate, by hydrolysis and condensation with hydrochloric acid, yielded 4·7 per cent. of furfur-

aldehyde, which, calculated on the original cellulose, is =7·57 per cent.

There is a similar change of constitution in the furfuroid groups, and this notwithstanding the fact that acetylation under the conditions selected is ascertained to involve the minimum of structural change; in the case of the β-cellulose of jute it is without influence on the furfuroid groups ("Researches on Cellulose," I., p. 130).

(b) *Hydrolysing Acids.*—The cellulose was treated with five times its weight of sulphuric acid dihydrate, $H_2SO_4,2H_2O$.

(1) After three hours at 18° the viscous solution was diluted so as to correspond with a concentration of 1 per cent. of the original cellulose.

The figures for furfuraldehyde were as follows:

	Furfuraldehyde.	
	Per cent.	Percentage of original.
Reprecipitated fraction (colloidal hydrate) (23 per cent.)	4·6	1·06
Hydrolysed to soluble derivatives (77 per cent.)	8·6	6·62
Total		7·68

(2) In a second experiment, the whole of the resolved mixture was boiled with hydrochloric acid; an estimation of furfuraldehyde gave 7·5 per cent., calculated on the original cellulose.

(3) *Action of Sulphuric Acid Dihydrate on the Colloidal By-product (above).*—This concentrated form of furfuroid was similarly digested with the acid in the cold, and, after dilution, the solution was treated with hydrochloric acid as above, with the following result:

Furfuraldehyde { From original 50·0 per cent.
After digestion 31·1 ,,

Here also we obtain the same result, 60 per cent. only of the furfuroid groups surviving as such.

The cellulose was next submitted to the action of sulphuric acid trihydrate, $H_2SO_4,3H_2O$.

(1) It was digested at 18° with five times its weight of the acid. The reaction is of a different order, as shown by the following results:

	Furfuraldehyde	
	Per cent.	Percentage of original.
Mixture of undissolved and reprecipitated (78·4 per cent.)	1·5	1·17
Hydrolysed to soluble forms (21·6 per cent.)	34·9	7·70
Total		8·87

(2) The experiment was repeated, using a larger proportion of the acid, which gave a more advanced resolution, as evidenced by the production of a homogeneous, viscous solution. On precipitation, 77·5 per cent. of the original was obtained in the colloidal hydrated form; the soluble hydrolysed products also yielded, as before, 35 per cent. of furfuraldehyde.

(3) The effect of prolonging the digestion for six days at 15—18° was next examined, with the following results:

	Furfuraldehyde	
	Per cent.	Percentage of original.
Reprecipitated hydrated colloid (61 per cent.) ...	1·1	0·67
Hydrolysed to soluble derivatives (39 per cent.)	19·9	7·76
Total		8·43

It is clearly established by this study of the furfuroid groups of esparto, both of the cellulose and non-cellulose components, that they are in a labile and potentially transitional form, and further doubt is cast on the very usual assumption that these furfuraldehyde-yielding carbohydrates are pentosans. These results must also be reviewed in the light of the data of the foregoing paper by Miss Cunningham.

The variations of the primary factors of reaction, cellulose, as well as acids, were carefully designed to extend the basis of criticism; there are many directly consequent results, and conclusions which require no further discussion. *The main result is to restore the cellulose–dextrose relationship to the position of an open question and problem.* It is now once more and more positively emphasised that the supposed proofs of a lineal descent are of doubtful validity. It should be recognised that the intervening factor of the unexplored colloidal state is very seriously to be reckoned with, not only on an a priori criticism of the assumed constitution of cellulose as a complex of actual hexosan (or hexose–pentosan) groups, but for its evident influence on the whole of the reactions described in this and the foregoing paper.

Thus we have to account for the fixation of SO_4H (or SO_4) in stable union by reaction with sulphuric acid dihydrate; no such reaction would appear to be possible with a hexose or even with an anhydride. Rather as a matter of form, we have examined the behaviour of dextrose with these acids. There is no fixation of SO_4H and no development of acid function by any constituent hydroxyl group.

As regards the possibility of a reaction between sulphuric acid and an alcoholic hydroxyl group, there must be simultaneous resolution of the sulphuric acid dihydrate, which implies a considerable (endo) thermal effect. It is therefore necessary to make a thermal

study of the reaction, and this will be undertaken with other typical cases which are already under investigation.

The simplest interpretation of the reaction in the meantime is that the effect is initiated with groups of *the complex* containing oxygen of basic function in excess of that which characterises any hexose or hexose anhydride. A nucleus group of this order may very well derive its basicity from a special configuration due to the affinity strains of the colloidal system. That such exist and are brought into play by reactions of this order is shown by the changes produced in the furfuroid groups of the esparto cellulose by reactions of a by no means energetic character, and in the case of the normal celluloses by the changes which we have specially investigated in our study of the reaction with formic acid (T., 1911, **99**, 1450).

It is still undetermined whether the product is a true ester or an ester hydrate, the latter being the analogue of the salts formed by the interaction of the colloidal hydroxides of the metals and the acid in aqueous solutions. It is also undetermined whether the acidity of the derivatives in excess of that due to SO_4H is the result of migration of hydroxyl groups attending the reaction or a secondary effect due to the entrance of SO_4 residues into the complex. That the former is probable is shown in the results obtained by Ost and Wilkening (*Chem. Zeit.*, 1910, **34**, 461) in their endeavour to prove the total hydrolysis of cellulose to dextrose. There was an invariable production of acids of low molecular weight (volatile acids) in many cases in considerable proportions.

Since the researches of which this and the foregoing paper are sections are in progress, we limit ourselves to experimental records and a brief treatment of the theoretical points which are present difficulties, but also a definite forecast of lines of progress.

As our present main subject is esparto cellulose, we may perhaps be allowed to direct attention to the change of paper used in printing this Journal—as from January, 1918—from the esparto cellulose type to a paper composed of wood and cotton celluloses.

A main reason for this change is the special reactivity of esparto cellulose with arylamines and derivatives, as described above. Those directly responsible for the publication of the Journal have been in difficulties as regards paper supplies, and it was deemed opportune to take advantage of the position by considering the technical problems involved and adopting a standardised paper, free from the particular defect in question.

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[*Received, February 7th, 1918.*]

XXIII.—*The Constitution of the Disaccharides. Part II. Lactose and Melibiose.*

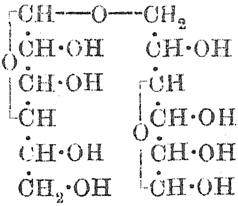
By Walter Norman Haworth and Grace Cumming Leitch.

Our present knowledge of the structure of the disaccharides is mainly restricted to the elementary facts that these sugars yield hydrolytic products which may be recognised and classified as one or other of the simple monosaccharides. Although many constitutional formulæ have been proposed for lactose, experimental work leading to the solution of this important problem has hitherto been lacking. Fischer's suggestion (*Ber.*, 1888, **21**, 2633) of the acetal type of linking of the two constituent hexoses cannot now be upheld, and the steady adherence of chemists within recent years to the γ-oxidic mode of representation of the hexoses further excludes formulæ based on the conception of these sugars as aldehydes (Fischer, *Ber.*, 1893, **26**, 2400; 1894, **27**, 2988).

That lactose is an anhydride of the two so-called aldo-hexoses, glucose and galactose, has long been known, and, inasmuch as it is also a reducing sugar, the active terminal group of one of the hexoses must necessarily be preserved in the structure of the disaccharide. Evidence is adduced on p. 192 showing that the reducing property which persists in lactose is attributable to the glucose residue, and that the similar property of the galactose residue has become latent by its combination with the glucose molecule. This mode of linking of the two hexoses, engaging as it does the reducing group of galactose, must therefore occur by combination of the latter with one of the hydroxyl groups of the glucose chain, and the allocation of the precise form and position of the linking constitutes the outstanding difficulty in assigning a definite formula to the disaccharide.

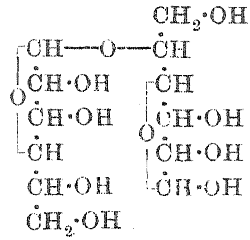
An important contribution to the study of lactose has been made by Ruff and Ollendorff (*Ber.*, 1900, **33**, 1802), and their conclusions are discussed in greater detail on p. 192 of this communication. Their researches have shown that the anhydride-linking of galactose with glucose does not concern the hydroxyl groups attached to the second and third carbon atoms from the reducing end of the glucose chain. If we are also to exclude the hydroxyl position next in order, on the ground of its being occupied already in the γ-oxide linking of the glucose structure, which is definitely known to be the case (p. 193), then there remain open to us two alternatives, namely, that the galactose-reducing group, in its union with the glucose, involves either the hydroxyl group attached to

the terminal carbon atom of the chain, or the adjacent penultimate hydroxyl group:



(Galactose residue.) (Glucose residue.)

(I.)



(Galactose residue.) (Glucose residue.)

(II.)

One or other of these formulæ must therefore represent both lactose and its synthetic stereochemical isomeride, *iso*lactose, and the final allocation of one of them to lactose and *iso*lactose leads to the inference that the alternative formula should be ascribed to melibiose, the disaccharide obtained by the partial hydrolysis of raffinose. We are now able to advance conclusive evidence in favour of the adoption of the second of these formulæ for lactose. Consequently, it follows that, according to our present knowledge of the chemistry of melibiose, formula (I) best represents the latter sugar. The possibility, however, that the hydroxyl group attached to the third carbon atom of the glucose residue is concerned in the linking with galactose in the melibiose molecule is not altogether excluded by the evidence available. In the case of lactose, no such dubiety remains.

This conclusion is of peculiar interest, apart from its relation to the solution of the immediate problem of the structure of lactose, in that it offers definite evidence of the hitherto unknown mode of linking of two sugar molecules in the form of a branched chain,

$$>CH\cdot O\cdot CH<\begin{matrix}CH_2\cdot OH\\ CH(OH)\end{matrix},$$

as shown in the lactose formula (II). Without some such hypothesis, it has always been a matter of difficulty to account for the numerous isomerides existing in the disaccharide series, and there can no longer be any reluctance in offering as an explanation of the occurrence of these isomerides the supposition that the reducing group of one hexose is united with a second residue through any one of the hydroxyl groups of the latter. Thus there are no fewer than four reducing disaccharides containing two glucose residues, namely, maltose, *iso*maltose, gentiobiose, and cellobiose, and the existence of these is explicable on the above grounds.

As an initial step in the investigation of the constitution of

lactose, experiments were instituted on the methylation of this sugar by the agency of methyl sulphate as alkylating medium, and a detailed description of the general applicability of this reagent in the sugar group has been given in a previous communication (Haworth, T., 1915, **107**, 8). The utility of methyl iodide and silver oxide for the methylation of sugars is confined to the non-reducing derivatives, such as the glucosides, since, in the presence of a reducing sugar, silver oxide functions as an oxidising agent, and esters of carboxylic acids are formed. This limitation imposed on the use of the earlier reagent has hitherto been an obstacle to the investigation of methylated disaccharides, inasmuch as the preparation of the methylglucosides of bioses is attended with considerable difficulty. Thus, as initial materials for an extended investigation, they are comparatively inaccessible.

With the view of determining the best experimental conditions for the direct methylation of reducing sugars, glucose was selected as an example. Methylation of the reducing group of the sugar proceeded by the aid of methyl sulphate and sodium hydroxide at a moderately low temperature, and methylation of all the hydroxyl positions was completed at a higher temperature. The crystalline product isolated in good yield was tetramethyl β-methylglucoside (see p. 195). Since this substance may be hydrolysed with greater ease than the α-modification, the present procedure is recommended as the best method of preparing tetramethyl glucose in quantity.

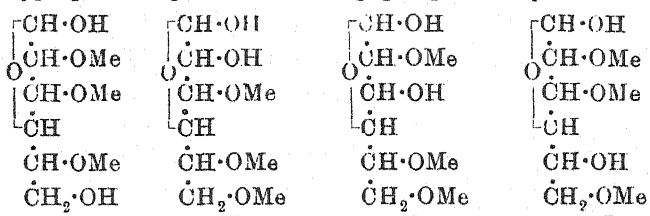
Conditions having now been established in the case of glucose, these were applied to the direct methylation of lactose, with satisfactory results. The eight hydroxyl positions in the disaccharide molecule were found to have been completely methylated, and heptamethyl methyllactoside was obtained in minute, colourless crystals melting at 77—82°, and showing a rotation of $[\alpha]_D$ $+5{\cdot}2°$ in water and $-16{\cdot}9°$ in ethyl alcohol. This crystalline variety, on the analogy of the glucose experiment, was probably the β-modification, and what is conceivably the α-form was also isolated as a colourless oil distilling at 210°/1·1 mm. Simultaneously, a quantity of hexamethyl methyllactoside was also prepared.

A portion of the heptamethyl methyllactoside was submitted to hydrolysis with 5 per cent. aqueous hydrochloric acid at 80°, and finally in the region of 100° for a brief period. Practically no hydrolytic cleavage occurred at a lower temperature than 80°. From the syrupy product two methylated hexoses were isolated, one of these being tetramethyl galactose, which was identified by conversion into the crystalline anilide melting at 192°, and showing the equilibrium value $[\alpha]_D$ $+38{\cdot}0°$ after catalysis. These data agree with those of the anilide of tetramethyl galactose prepared

by Irvine and McNicoll (T., 1910, **97**, 1454), and, moreover, a mixed melting-point determination proved the identity of the present specimen, derived from methylated lactose, with a specimen provided by the above authors.

Complete separation of the methylated galactose fragment having been effected through conversion into the anilide, the remaining syrup, on keeping in a desiccator, crystallised in minute needles. The latter compound, melting at 118—119°, was shown to be a trimethyl hexose and represented the glucose fragment from the hydrolysis of the lactoside. Its stability towards permanganate indicated that it belonged to the butylene oxide type of sugars. Since eight methoxyl groups were originally present in the heptamethyl methyllactoside, and four of the methoxyl groups have been acounted for by the isolation of the tetramethyl galactose fragment, whilst one methoxyl group was removed as the glucosidic group, there remain only three other methoxyl groups to be allocated. These could only have been present in the glucose fragment, and thus the isolation of the trimethyl hexose establishes its identity as a trimethyl glucose.

There are possible only four trimethyl glucoses of the butylene oxide type possessing a free reducing group, namely:



(III.) (IV.) (V.) (VI.)

The trimethyl glucose isolated in the present case does not form an osazone, and thus formula IV is excluded on these grounds. Again, the trimethyl glucose of formula III is known, and this is a liquid having a different rotation from that of the substance now isolated (Purdie and Bridgett, T., 1903, **83**, 1039).* The choice of a formula for the crystalline trimethyl glucose obtained from heptamethyl methyllactoside is thus restricted to formulæ V and VI. Fortunately, by having regard to the behaviour of lactose itself, we are able to decide between these two alternatives. Lactose gives rise to a phenylosazone, and also may be made to undergo oxidation with bromine water to lactobionic acid (VIII). By hydrolysis of the latter, Fischer and Meyer obtained gluconic acid and galactose (*Ber.*, 1889, **22**, 361), and from the former

* The constitution originally assigned to this liquid trimethyl glucose has recently been confirmed by Irvine and Dick (unpublished research).

glucosone and galactose were isolated as cleavage products (Fischer, *Ber.*, 1888, **21**, 2633).

From these facts, it is clear, first, that in lactose the reducing group of the glucose residue is free; secondly, that the hydroxyl group adjacent to this reducing group is also free:

$$
\begin{array}{llll}
 & CH_2\cdot OH \ldots\ldots & 6 & \\
C_6H_{11}O_5\!-\!O\!-\! & \dot{C}H \ldots\ldots\ldots & 5 & \\
 & \dot{C}H \ldots\ldots\ldots & 4 & \\
 & \dot{C}H\cdot OH \ldots\ldots & 3 & \longrightarrow \\
 & \dot{C}H\cdot OH \ldots\ldots & 2 & \\
 & \dot{C}H\cdot OH \ldots\ldots & 1 &
\end{array}
\qquad
\begin{array}{ll}
 & CH_2\cdot OH \\
C_6H_{11}O_5\!-\!O\!-\! & \dot{C}H \\
 & \dot{C}H\cdot OH \\
 & \dot{C}H\cdot OH \\
 & \dot{C}H\cdot OH \\
 & \dot{C}O\cdot OH
\end{array}
$$

(Galactose residue.) (Glucose residue.) (VII.) (Lactose.)*

(Gluconic acid residue.) (VIII.) (Lactobionic acid.

Again, Ruff and Ollendorff (*loc. cit.*) were able to degrade lactose to the galacto-arabinose by oxidising the calcium salt of lactobionic acid with Fenton's reagent. The syrupy sugar was found to yield on hydrolysis *d*-galactose and *d*-arabinose, and therefore was a hexose–pentose complex, isomeric with vicianose. This compound readily formed a phenylosazone, and therefore the hydroxyl group adjacent to the reducing group of the arabinose residue must be free; hence it is proved that two of the secondary alcohol groups which are situated nearest to the reducing group in the original lactose molecule must be free, that is, the hydroxyl groups attached to the carbon atoms numbered 2 and 3 in formula VII, since the carbon atom marked 1 is eliminated by the process of degradation. The consideration of formula V as representing the constitution of the trimethyl glucose fragment is thus precluded:

$$
\underset{\text{Lactose.}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{Galacto-arabinose.}}{C_{11}H_{20}O_{10}} \longrightarrow \underset{\text{Galactose.}}{C_6H_{12}O_6} + \underset{\text{Arabinose.}}{C_5H_{10}O_5}
$$

$$\downarrow$$

Osazone.

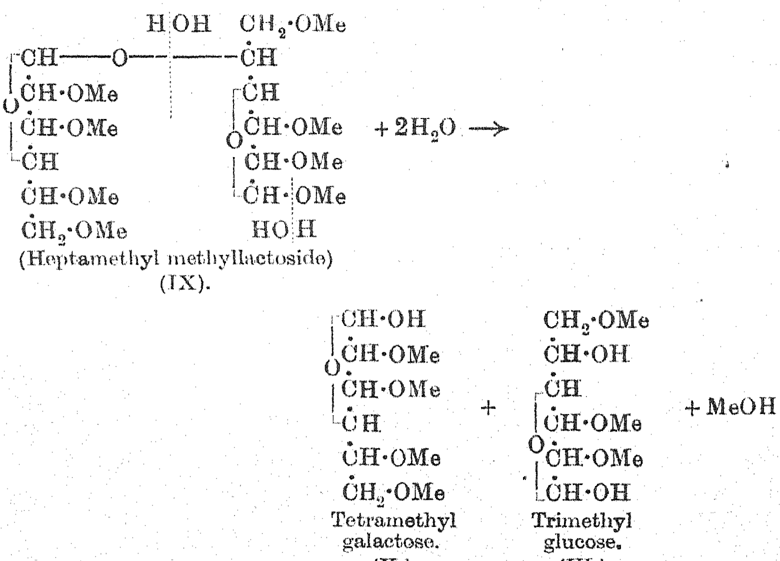
This result leaves open only three possible positions for the coupling of the galactose residue with glucose in the lactose molecule, namely, the secondary alcohol groups attached to the fourth and fifth carbon atoms and the terminal primary alcohol group of the glucose chain (see formula VII, above).

In the course of the present investigation it has been shown

* In elucidating these transformations the structural formula for lactose determined in the course of the present communication is used throughout. In order to simplify reference, numbers are ascribed to the different positions in the sugar chain.

that the trimethyl glucose fragment, obtained on hydrolysis of heptamethyl methyllactoside, is of the butylene oxide type, and thus the secondary alcohol group of the fourth carbon atom of the glucose chain is occupied by this butylene oxide linking. Further, as already stated (p. 191), evidence is available that this trimethyl glucose cannot be represented by formula III, and thus the primary alcohol group cannot have been concerned in the galactose coupling. As formulæ IV and V given above are also excluded by experimental evidence, there remains, then, the only other possibility, namely, that the trimethyl glucose isolated from the hydrolysis of heptamethyl methyllactoside has the constitution represented by formula VI.

Since this is so, it follows that the constitution of lactose is also clearly indicated: in the disaccharide the galactose residue is combined through its reducing group with the glucose residue, and involves in this union the secondary alcohol group attached to the fifth carbon atom of the glucose chain, for the latter grouping remains unprotected by a methyl group in the trimethyl glucose isolated, and must consequently have been concerned in the disaccharide linking in the completely methylated lactose. The hydrolysis of heptamethyl methyllactoside may thus be formulated as below, the dotted lines indicating the points of cleavage:



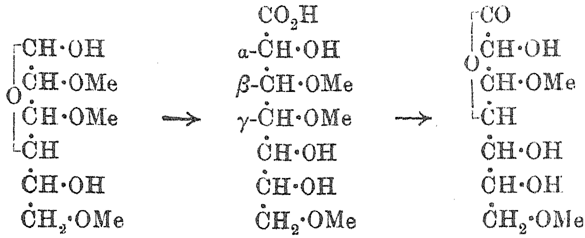
(Heptamethyl methyllactoside) (IX).

Tetramethyl galactose. (X.)

Trimethyl glucose. (VI.)

A trimethyl glucose, identical with that obtained from lactose in the course of this work, was also isolated by Denham and Wood-

house from methylated cellulose (see p. 199). This has the same crystalline form, its melting point is not depressed by mixing the two specimens, and it possesses the same equilibrium rotation value.



(XI.) (XII.) (XIII.)

These workers prepared from it the trimethyl heptonic acid (XII) by ascending the series, and showed that this acid only undergoes lactone-formation at the expense of the loss of a methyl group (XIII). The methyl group eliminated by the lactonisation was considered by the authors to be that having the γ-position, and the constitution they tentatively ascribed to the trimethyl glucose is represented by formula XI, which is identical with formula VI (p. 191).

We are thus able to confirm the structure assigned to this trimethyl glucose, and it is of interest that the same mode of dihexose linking that occurs in cellulose is also present in lactose.

Since lactose is hydrolysed by lactase, which is the specific enzyme for β-galactosides, just as emulsin is the enzyme for β-glucosides, therefore the two known forms of α- and β-lactose are to be regarded as the α- and β-glucose-β-galactosides. Presumably the synthetic *iso*lactose, concerning which little is known chemically, is the stereoisomeric glucose-α-galactoside, whilst melibiose may be considered to be the structurally isomeric glucose-β-galactoside possessing the constitution I (p. 189).

EXPERIMENTAL.

Preparation of Tetramethyl β-Methylglucoside.

For the purpose of this preparation, 27 grams of glucose were dissolved in 10 c.c. of water. There were also required 142 grams of methyl sulphate (109 c.c.) and a solution containing 109 grams of sodium hydroxide in 190 c.c. of water. One-fifth of the above volume of methyl sulphate was added immediately to the glucose solution, and the temperature of the mixture maintained at 35° by surrounding the vessel with warm water. From a dropping funnel, 38 c.c. of the sodium hydroxide solution were introduced slowly, drop by drop, with efficient mechanical stirring. There-

after the temperature was raised to 40°, and then, gradually, over a period of three hours to 60°.

By this time the glucose was almost completely converted into β-methylglucoside. The temperature was now maintained at 60° while the remainder of the sodium hydroxide solution and methyl sulphate was slowly added in approximately equivalent amounts in unit time from two dropping funnels, the mixture being meanwhile vigorously stirred.

When the whole of the reagents had been added, the temperature was raised to 100°, and, after keeping for half an hour at this temperature the reaction was complete. On cooling, the aqueous solution was extracted with chloroform, the extract dried, and the product distilled. Almost the whole of the residue remaining after the removal of the solvent distilled at 108—110°/0·23 mm. as a colourless oil having n_D 1·4455. Other fractions distilling up to 150° were small in amount and had refractive indices varying from 1·4495 to 1·4708, and these consisted of partly methylated glucosides. The first fraction crystallised instantly on nucleation with a crystal of tetramethyl β-methylglucoside, which had previously been prepared by Purdie and Irvine (T., 1904, **85**, 1064), and the crystals, after draining on porous tile, melted at 39—41°. A mixed melting-point determination with the specimen previously prepared by the older method showed no depression. The rotation of the substance in absolute ethyl alcohol was $[\alpha]_D$ $-13·3°$ ($c=5·0$). The following analytical data were determined:

0·1347 gave 0·6125 AgI. OMe = 60·03.

$C_6H_7O(OMe)_5$ requires OMe = 62·0 per cent.

The Complete Methylation of Lactose.

Isolation of Hexamethyl Methyllactoside and Heptamethyl Methyllactoside.

A convenient method of conducting the methylation of a disaccharide may be illustrated by the use of lactose. The materials were used in the following proportions: lactose (30 grams), methyl sulphate (114 c.c.), sodium hydroxide (111 grams), dissolved in water (210 c.c.). The lactose was dissolved in the minimum amount of hot water and the solution cooled to 30°. One-eighth of the above volume of methyl sulphate was added, followed by one-eighth of the total volume of the sodium hydroxide solution. The latter reagent was added very slowly with mechanical stirring, and the temperature of the mixture maintained at 30° by means of a water-bath.

This treatment was repeated, one-eighth of the original volume

of methyl sulphate being mixed with the lactose solution, and again one-eighth of the sodium hydroxide solution slowly introduced, while the temperature was maintained at 40°.

The mixture was kept overnight, and on the following day the reducing property of the free sugar was found to have disappeared. It is important that throughout all these operations no free alkalinity should be allowed to develop, otherwise scission of the disaccharide occurs. Thereafter the temperature was raised to 60°, and a third proportion corresponding with one-eighth of the original volume of methyl sulphate was introduced, and a similar proportion of sodium hydroxide solution was added, drop by drop, with vigorous stirring. The remainder of the reagents was added at 70° in the same order and in similar fractions, stirring being continued throughout the addition. Finally, the temperature was raised to 100° for a period of half an hour, when the reaction seemed to be complete. Extraction of the product was carried out with chloroform, the extract dried, and the solvent distilled. A residue was obtained which yielded four fractions on distillation:

I.	160–193°/0·2 mm.	
II.	193°/0·22 mm.	n_D 1·4759.
III.	204–210°/0·38 mm.	n_D 1·4760.
IV.	217°/0·63 mm.	

The third fraction, on analysis, gave results agreeing with the formula of hexamethyl methyllactoside:

0·1955 gave 0·7190 AgI. OMe=48·55.

$C_{12}H_{15}O_4(OMe)_7$ requires OMe=49·32 per cent.

0·1308 gave 0·2450 CO_2 and 0·0969 H_2O. C=51·1; H=8·23.

$C_{19}H_{36}O_{11}$ requires C=51·8; H=8·20 per cent.

A determination of the optical activity of this fraction in water gave $[\alpha]_D + 7·47°$ (c=4·28), and this value shows a considerable diminution in the specific rotation of the original lactose ($[\alpha]_D + 52·2°$).

When the material represented by the fractions I—IV was twice further methylated, either with methyl sulphate and sodium hydroxide, or, alternatively, with silver oxide and methyl iodide, it was found that the bulk of the product consisted of heptamethyl methyllactoside, as shown below. This was submitted to distillation under diminished pressure by means of the Gaede pump.

Fraction I.	185°/0·05 mm.	n_D 1·4559.
Fraction II.	195°/0·05 mm.	n_D 1·4688.
Fraction III.	200°/0·05 mm.	n_D 1·4713.

Fractions I and III were exceedingly small in amount.

The main fraction gave the following analytical data:

0·0586 gave 0·2363 AgI. OMe = 53·34.
$C_{12}H_{14}O_3(OMe)_8$ requires OMe = 54·63 per cent.

0·1352 gave 0·2585 CO_2 and 0·1025 H_2O. C = 52·16; H = 8·43.
$C_{20}H_{38}O_{11}$ requires C = 52·83; H = 8·43 per cent.

It was observed that this major fraction (II) crystallised on keeping, and especially on triturating with light petroleum. The crystals were drained on porous porcelain and recrystallised from light petroleum.

The colourless needles melted at 77—82°, and a determination of the refractive index of the superfused solid gave n_D 1·4675.

Complete analytical data were now obtained for the crystalline specimen:

0·1002 gave 0·4175 AgI. OMe = 55·0.
$C_{12}H_{14}O_3(OMe)_8$ requires OMe = 54·63 per cent.

0·1281 gave 0·2482 CO_2 and 0·0974 H_2O. C = 52·84; H = 8·44.
$C_{20}H_{38}O_{11}$ requires C = 52·83; H = 8·43 per cent.

and the rotation of this pure specimen of heptamethyl methyllactoside was determined in different solvents:

Rotations: I. Water $[\alpha]_D$ +5·19°; c = 0·771.
II. Absolute ethyl alcohol −16·87°; c = 1·482.
III. Methyl alcohol −13·04°; c = 1·459.
IV. Acetone −13·64°; c = 1·1466.

Hydrolysis of Heptamethyl Methyllactoside.

Preliminary experiments on the hydrolytic cleavage of this completely methylated lactoside showed that the hydrolysis occurred probably in two stages. With 5 per cent. aqueous hydrochloric acid, after two and a-half hours' heating at 80°, scission of the disaccharide linking takes place, and the specific rotation at this point is of the order of $[\alpha]_D$ + 66°. Prolonged heating at this temperature, or a short period of heating at 98°, results in the removal of the methylglucoside linking, and the specific rotation registered is about $[\alpha]_D$ + 76°. A larger quantity of material was then subjected to similar treatment, and the product, consisting of a mixture of methylated hexoses, was separated into its individual components in the following way. The aqueous hydrochloric acid solution was neutralised with barium carbonate and evaporated to small bulk in a vacuum. The syrupy residue was extracted with ether to remove mineral salts, and, after filtration from these, the ethereal solution was evaporated. It was anticipated that the methylated hexoses derived from this hydrolysis would be (1) a tetramethyl galactose, (2) a trimethyl glucose. The former of

these may be expected to possess solubilities differing from those of the latter, owing to its containing fewer free hydroxyl groups. Ultimately it was seen that a separation of the methylated galactose and glucose fragments could be effected by taking advantage of the insolubility of the anilide of tetramethyl galactose in water, the anilide of the other methylated hexose present being soluble. The dried, syrupy residue above mentioned was therefore digested with an alcoholic solution containing excess of aniline (7 molecular proportions) for three hours. On cooling, colourless crystals of an anilide separated. The whole of the mixture was subjected to steam distillation in order to remove the excess of aniline, and from the undistilled residue there separated crystals of crude anilide. Thus, in one experiment, from 2·55 grams of hydrolysed syrup 1·2 grams of crystalline anilide were obtained. This was filtered and recrystallised from ethyl acetate, when long, silky, colourless needles, which matted together on filtration, were obtained melting at 192° without decomposition. Polarimetric examination of the anilide in acetone solution gave $[\alpha]_D +38{\cdot}0°$ as the equilibrium value after catalysis. These data agree with those of the anilide of tetramethyl galactose prepared by Irvine and McNicoll (T., 1910, **97**, 1454).

A mixture of the above anilide with a specimen prepared by the latter authors showed no depression in melting point, and thus there can be no doubt of their identity.

On another occasion a highly purified specimen of the anilide was isolated in this way from the products of hydrolysis, and more accurate optical data were obtainable. These may now be given as $[\alpha]_D$, initial value $-83{\cdot}3°$, falling to the permanent equilibrium value $[\alpha]_D +40{\cdot}7°$.

The filtrate from the crystalline anilide contained in solution another anilide, presumably that of the methylated glucose fragment. The addition of a trace of mineral acid caused the separation of aniline, which was removed by distillation in a current of steam, and the residual solution was concentrated in a vacuum at 20°. A moist syrup remained behind which weighed 1·3 grams; this was dried by solution in absolute alcohol, the solvent distilled, and from the residual syrup there separated minute needles which, after recrystallisation from dry ether, melted at 118—119°. The sparing solubility in dry ether of this colourless substance, its stability towards permanganate, and its melting point indicated that it was probably identical with the trimethyl glucose obtained by Denham and Woodhouse from methylated cellulose (T., 1914, **105**, 2364; 1917, **111**, 244). Confirmation on this point was forthcoming, as for the purpose of comparison we were able, by

the courtesy of these authors, to obtain a specimen of the trimethyl glucose prepared by them. This specimen, which had been kept for some months, was found to melt at 114°, but after recrystallisation it melted at 117°. The solubilities, crystalline form, and melting point of this recrystallised specimen, and also a mixed melting-point determination (117—118°), proved the identity of the two specimens, so that there can be no doubt that the colourless, crystalline substance obtained as the second cleavage product of heptamethyl methyllactoside is a trimethyl glucose.

The initial value for the specific rotation in methyl alcohol was determined, namely, $[\alpha]_D + 112{\cdot}9°$; after catalysis with a trace of hydrochloric acid, the reading diminished to an equilibrium value $[\alpha]_D + 69{\cdot}1°$. It will be seen that the initial rotation recorded is slightly higher than the value ($[\alpha]_D + 103{\cdot}9°$) quoted by Denham and Woodhouse (*loc. cit.*), whilst the equilibrium value is almost identical with that quoted by them for an acetone solution of the substance (69·5°). This slight variation in the magnitude of the initial rotation may be explicable on the ground that the melting point found by ourselves is 8° higher than that quoted by the former authors in their communication, so that from methylated lactose the compound may be more readily obtainable as a pure stereochemical form. The crystalline compound combines with phenylhydrazine in the cold, giving an oily phenylhydrazone, but no phenylosazone derivative could be prepared.

We can also confirm the constitution assigned to this compound, and a discussion of the formula (VI) is included in the theoretical part of this communication.

We acknowledge our indebtedness to the Carnegie Trust for a scholarship which has enabled one of the authors to collaborate in this investigation.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

[*Received, February* 28th, **1918.**]

Recent Studies on Active Nitrogen.

A Lecture delivered before the Chemical Society on February 21st, 1918.

By the Hon. ROBERT JOHN STRUTT.

IN 1913 I gave a Friday evening lecture at the Royal Institution, in which some of the more striking phenomena of active nitrogen were exhibited. This evening I shall dwell chiefly on results obtained since that time, but to be intelligible to those coming fresh to the subject, it will be necessary to traverse a little of the old ground.

The fundamental experiment on this subject is to pass a stream of rarefied nitrogen through a discharge tube *a* (Fig. 1) in which a vigorous jar discharge is maintained. The stream of gas, drawn by a powerful air pump, issues into the vessel *b*, where it exhibits a brilliant yellow light. The fact that no electric discharge passes in *b* and that the gas takes an appreciable time to pass through this vessel shows that it remains glowing after the electric discharge is over, and this may be established very directly by simply turning the exciting discharge off, when the luminosity will be seen to persist for some seconds' interval flowing down into the pump. Indeed, in favourable circumstances and with a closed vessel scrupulously clean, the luminosity persists for several minutes.

Evidently this luminosity (which is not of the nature of temperature-radiation) can only be maintained by the passage of the nitrogen gas from a state in which it contains more potential energy to a state in which it contains less. This circumstance alone might suggest that a special modification of nitrogen is present, but this becomes a certainty when we note the behaviour of the glowing gas when other gaseous substances are brought in contact with it. For it is found that hydrocarbons are converted at the ordinary temperature into hydrocyanic acid, and that the more volatile metallic vapours are converted into nitrides.

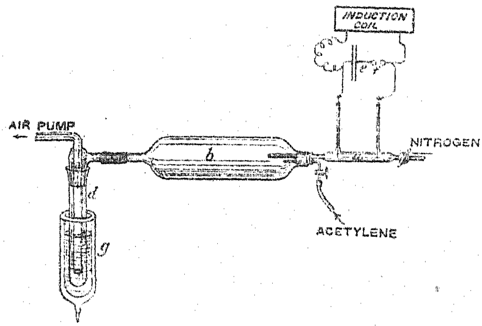
Ordinary nitrogen will certainly not behave in this way, and therefore it does not seem over-bold to assume that an extraordinary kind of nitrogen is present. This has been named, with a minimum of hypothesis, active nitrogen. So far as I am aware, no alternative interpretation of the facts mentioned has been attempted.

In some of the developments of radioactivity, it has been an unfortunate necessity to work with quantities so small that often

they could not be weighed or even seen. It may be remarked in passing that whatever legitimate scepticism may have been felt about results so attained, at any rate they have led to conclusions which can be verified by the well-tried methods of the chemical analyst. It suffices to refer to the now established fact that there are various kinds of lead of different atomic weights.

There is, or has been, an idea abroad that my conclusions on active nitrogen are dependent on similar indirect methods: that the evidence for the existence of an active modification of nitrogen depends on a dubious interpretation of obscure spectroscopic phenomena. I hope this evening to make it quite clear that this is not the case. In fact, I should not have had the courage to face you to-night if I had not had more direct and convincing evidence to offer. I wish to emphasise that the existence of active nitrogen was formulated solely on the grounds which appeal most directly

FIG 1.



to chemists. The properties of this substance have been examined by the ordinary methods of chemical analysis, carried out in many cases, not on a microscopic scale, but in vessels of ordinary or even large size, dense precipitates and strong colorations being obtained such as do not require the eye of faith for their recognition.

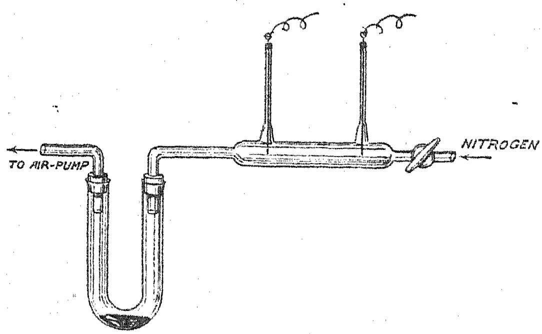
Although the luminous phenomena accompanying these actions form no part of the evidence for the existence of the active substance, yet they are of considerable interest in connexion with its properties, and I shall have a good deal to say about them.

I first show you the action of active nitrogen on acetylene. When acetylene enters the stream of yellow, glowing gas, you see that a lilac tint is developed. This shows the well-known cyanogen spectrum—the spectrum obtained, for instance, from burning cyanogen; and it was for this reason that it was first suspected that hydrocyanic acid was formed. It would, however, be most

unsatisfactory to rely on such an argument. I do not, and never did rely on it. In showing the presence of hydrocyanic acid, I have generally frozen it out from the gas stream with liquid air (as in Fig. 1) and shown its presence chemically in the cooled vessel *d*. To-night, however, a simpler method must suffice. We lead the gas ejected by the pump through a solution of sodium hydroxide to collect the hydrocyanic acid. On adding a mixture of ferrous and ferric salts, and acidifying, you see that a strong Prussian-blue reaction is obtained.

I have shown on previous occasions the action of active nitrogen on mercury vapour. Mercury was gently heated in a stream of the yellow, glowing gas, and it was found that the yellow glow was displaced by the green light of mercury, familiar in the mercury vapour lamp, with its characteristic line spectrum. At the same time, a nitride is produced. This may be treated with water, when

FIG. 2.



ammonia is formed, and the Nessler reaction is obtained. The nitride is unstable, and when heated pretty strongly it decomposes with minute flashes, accompanied by audible crackling.

I shall now perform a novel experiment, not before shown publicly. This is the action of active nitrogen on cold liquid mercury. The stream of glowing gas is led over a U-tube (Fig. 2) containing a small quantity of clean mercury, not enough to fill the bottom bend of the tube. So long as the tube is at rest nothing happens, the glowing gas passing on; but if the tube is shaken so as to break the skin of the mercury surface, and constantly to renew it, it is seen that the mercury is quickly attacked and becomes foul, very much after the fashion in which it is made foul by ozone. At the same time, the luminosity of the issuing gas is extinguished, showing that it is no longer in the peculiar state.

Let us now take some of the mercury which has been made foul

in this way, mix it with water, distil off a portion, and test with Nessler's solution. You will have no difficulty in recognising the presence of ammonia, showing that a nitride had been formed.

One interesting point is that when liquid mercury is employed in this way we do not get any trace of the mercury spectrum, so conspicuous when active nitrogen mingles with mercury vapour, but the chemical reaction occurs none the less. Thus it appears that we cannot trace any close or necessary connexion between the luminous effects and the chemical ones.

I will now direct your attention to another interesting case of this kind. Suppose that nitrogen is purified by allowing it to remain over cold phosphorus, and then thoroughly dried by passage through long and tightly packed tubes filled with phosphoric oxide. In these circumstances, it will be tolerably free from traces of oxygen compounds, and the afterglow of the gas, usually yellow, will be found to be practically invisible through a blue glass. Suppose now that we allow a small quantity of almost any oxygen-containing gas to flow into the stream of glowing nitrogen, taking care, however, to prevent it from mixing with the nitrogen until the latter has left the discharge. Nothing particular seems to happen when the oxygen compound flows in, so long as we observe the yellow light directly, except that the yellow light fades out sooner; but if a blue glass is interposed to cut out the yellow light, then we see that at the confluence a bluish-violet light is developed by admixture of the gases. This bluish-violet light is to a great extent masked by the yellow when no colour-filter is used.

The same thing can be recorded photographically, using first an isochromatic plate with yellow screen, then an ordinary plate with a blue screen.*

Oxygen itself, or carbon monoxide or dioxide, or nitrous or nitric oxides, will give this effect when introduced into the yellow-glowing gas. I wish you particularly to notice that in these experiments the admixture does not get back to the discharge tube. It never comes in contact with the electric discharge at all. Only nitrogen goes through the discharge. The oxygen-containing gas is mixed with it afterwards.

The yellow light when spectroscopically analysed shows a selection of the bands produced by nitrogen in a vacuum discharge, although omitting many of them in a very strange way. It is simply a nitrogen spectrum. But what of the bluish-violet light? Although I have spoken of it as bluish-violet, it is really in the main ultra-violet, and it consists of two sets of bands, which have

* Or no screen at all, for the photographic action of the yellow light in the latter case is relatively too weak to be worth considering.

been called, for the sake of distinction, the β- and γ-groups of bands. The β-bands are not at present known to be produced in any other way, but the γ-bands occur when oxides of nitrogen (nitrous or nitric) are introduced into a Bunsen flame. They do not occur in a Bunsen flame burning in the ordinary way, which, of course, contains oxygen and nitrogen separately, and these facts, taken together, would seem to suggest very distinctly that the spectrum in question indicates oxidation of nitrogen. Is there, then, any oxidation when oxygen is led into active nitrogen, and this spectrum results? Careful tests of the products with the extremely sensitive tests available (Griess's reagent) have convinced me that no oxides of nitrogen are produced. I have been reluctant to accept this conclusion, and have returned again and again to the subject, always with the same result. It would have been satisfactory to find that the isolation of active nitrogen would help us to understand the processes occurring in the arc process for oxidising nitrogen, and it is still possible that something of the kind may be made out. Koenig and Elöd in Germany have stated that a particular kind of active oxygen (not ozone) can be produced by electric discharge which will unite directly with active nitrogen. I have attempted to repeat these experiments, but have hitherto been unable to satisfy myself of their correctness. I do not wish, however, to speak too positively on the subject.

However this may be, it is remarkable that whilst active nitrogen will attack carbon compounds, even methane, to form hydrocyanic acid, it will not react either with oxygen or with hydrogen.

Hitherto, we have considered chiefly the properties of active nitrogen when formed. It is also of interest to consider the conditions for its formation. These present many puzzling problems, and in this connexion I shall have to content myself chiefly with recording facts rather than theories.

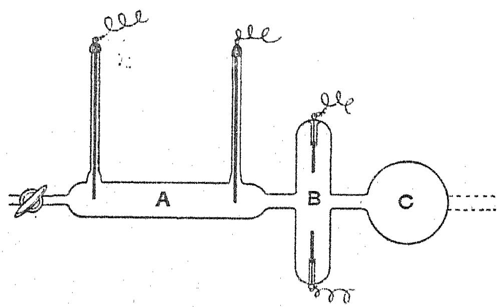
Let us first consider what kind of electrical conditions are best. In the first place, it is far preferable to work at a low gaseous pressure, a few mm. of mercury. The reason for this seems to be that collision with ordinary nitrogen molecules tends in some way to the destruction of active nitrogen, although how this occurs is not clear.

The next point is that a Leyden jar discharge is much preferable to the discharge of an induction coil without a jar. As is well known, the effect of the jar is to store up electricity and allow it to discharge suddenly through the gas. In these circumstances, the momentary current density is very high, and the nature of the discharge is altered in other respects: the peculiar phenomena of negative dark space and negative glow are obliterated, and the

spectrum of the light along the length of the discharge is modified, losing its reddish colour and becoming much bluer. At the same time, the production of active nitrogen is much increased. Accordingly, the jar discharge is generally used in experiments on active nitrogen.

Not only is the jar discharge the best, but if an uncondensed discharge (without jar) passes through the gas after a jar discharge, it is positively destructive, undoing part of the work which has been done by the jar discharge. This is illustrated by the experiment of Fig. 3. We allow a stream of the rarefied nitrogen to pass in succession through the discharge tubes *A* and *B* and the observation vessel *C*. The jar discharge passing in *A* produces active nitrogen, recognised by the orange glow. If we start an uncondensed discharge in *B*, leaving other conditions unchanged, the

FIG. 3.



brilliancy of the glow in *C* is diminished, proving the destructive effect above referred to.

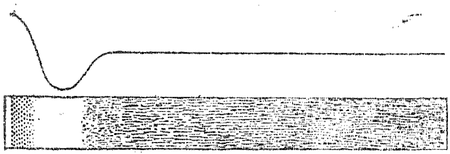
This and other evidence proves that the production of active nitrogen by the discharge is of the nature of a reversible reaction. The concentration only attains a certain limit, which may be lowered if the conditions become less favourable.

We may consider the analogy of this to better known cases of the production of endothermic substances. Consider, for instance, the known production of ozone from oxygen by the action of a high temperature. The concentration of ozone increases with the temperature of the hot tube, and the object is to cool the hot gases as quickly as possible, so as to preserve the concentration characteristic of a high temperature. If we subsequently passed the ozonised oxygen through a less strongly heated tube, we should find the concentration lowered thereby. In directing attention to this analogy, I do not wish to commit myself to the view that the action of the discharge is necessarily due to high temperature. There

are many doubts and obscurities overshadowing any theory of that kind.

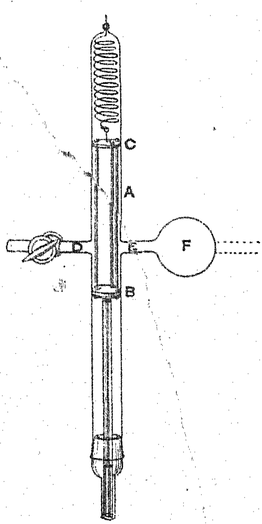
Although, as we have seen, the condensed discharge is the most efficient for activation of nitrogen, it is worth while to go back for a moment to the uncondensed discharge, or steady current through

Fig. 4.



the gas, produced preferably by means of a high-tension continuous-current dynamo. In this case, the discharge presents several distinct features. There is the Crookes's dark space near the cathode, the blue negative glow, gradually fading off to the darkness of the Faraday dark space, and then the red, positive column extending to the anode. These features are indicated in the slide (Fig. 4). We may draw a current of nitrogen transversely across any part of this discharge (the apparatus used is shown in Fig. 5) and obtain activation. As might be expected, the intensity of activation is not the same in the different parts of the discharge. The ordinates of the curve drawn above the figure of the discharge tube show the comparative intensities in the different parts of the tube, and it will be seen that the blue negative glow, particularly in the immediate neighbourhood of the cathode, is the part of the discharge where activation is strongest. It is worth noticing, and may be significant, that the bluer kind of discharge, whether obtained by approaching the cathode or by introducing a Leyden jar, is the more efficient in producing active nitrogen.

Fig. 5.



Much more might be said about the electrical conditions for producing active nitrogen, but I will pass to what, from the chemical point of view, may be of more interest. In the Royal Institution lecture in 1913, which has been mentioned, I referred to certain conclusions which Comte, and also Tiede and Domcke,

had reached in Germany. Their conclusion was that the phenomena which I had described in connexion with active nitrogen did not occur unless the gas contained traces of oxygen, and the last two authors went so far as to conclude from this that there was no such thing as active nitrogen. I said at the time that I was satisfied they were entirely mistaken as to the necessity for oxygen; but I now recognise that I spoke over confidently, and that this was too strong an expression to use. I think you will agree with me that the experiments I have shown you this evening on the formation of hydrocyanic acid and of nitrides are not easy of interpretation if the existence of active nitrogen is denied; but there was this much of truth in Tiede and Domcke's conclusion—that very pure nitrogen does not yield active nitrogen under the influence of the discharge, and that a trace of oxygen added will make it do so. What they did not discover, but what I have found since, is that a trace of almost any admixture will have the same effect. For instance, a trace of methane or ethylene will do it, or, again, carbon dioxide, or carbon monoxide, or hydrogen sulphide, or mercury vapour. In the experiments on which I relied when I denied the validity of Tiede and Domcke's work, my attention was concentrated on the removal of any trace of free oxygen; this did not result in reducing the glow, and I now appreciate that this was because other impurities were present. I was right in denying that oxygen was essential, but I was wrong in saying that pure nitrogen was all that was needed.

The method which I have generally used for preparing nitrogen is to take the commercial compressed gas, prepared by the rectification of liquid air, and to store it over water in a gas holder, in which is hung up a perforated metal bucket containing phosphorus. Gas prepared in this way always gives active nitrogen freely. To begin with, it is moist. I have always dried it with an ordinary tube of phosphoric oxide, but if the spectrum of the glow is photographed, it still shows the β- and γ-groups of bands characteristic of oxygen compounds present in active nitrogen. Passage over very long tubes tightly packed with granular phosphoric oxide reduces the intensity of these bands almost to the vanishing point.

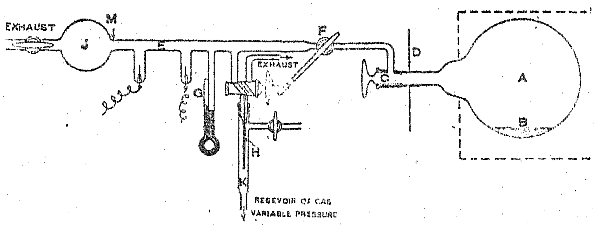
When they disappear, however, another impurity is unmasked, for the violet and ultra-violet bands characteristic of cyanogen compounds appear, showing that hydrocarbons are present, and react with the active nitrogen to yield this spectrum. I have tried to get rid of these cyanogen bands by employing specially pure phosphorus, which I owe to the kindness of Mr. Albright, but without success. We cannot get pure nitrogen by this method,

although it is fairly successful in removing oxygen and oxygen compounds.

I have not hit on any really convenient plan for getting nitrogen so free from impurities that it does not yield active nitrogen. The method that has served me best is to heat the commercial gas in a globe of 4 litres capacity for many hours at 300° with metallic sodium. It is desirable, if not absolutely necessary, to avoid using sodium which has been stored in oil, and thus contaminated with hydrocarbons. The globe once set up serves for repeated charges of nitrogen, and seems to perform better after it has been used repeatedly.

Hot sodium has the advantage of destroying nearly all the impurities that might be present in the nitrogen, for example, oxygen, water vapour, carbon dioxide, hydrocarbons. Hydrogen, it is true, is apt to be liberated, but this for the present purpose is comparatively unimportant. Gas taken from the globe *A* (Fig. 6) (which is allowed to cool after the purifying process is

Fig. 6.



over) is led through the discharge tube *E* and the bulb *J*, when, if any active nitrogen is produced, we shall see the characteristic glow. The glow from the gas purified in this way may be got very faint, verging on invisibility, and we can then restore it by admission of a suitable impurity in very minute amount through the capillary tube *H*. The exact manipulation in connexion with this admission of the gas need not detain us now; I have described it in one of my Royal Society papers. The general method is to increase the feed at the outer end of the capillary from low pressure towards atmospheric pressure until the effect becomes appreciable.

The flow of nitrogen was regulated by hand, so as to maintain a rate of 2·6 litres per hour, and the tributary stream through the fine capillary could be compared with this, so as to show what fraction of impurity was being added. With oxygen, for instance, the effect was perceptible with a tributary stream of 1 c.c. per hour, and 3·5 c.c. produced the maximum effect. In the latter case, the oxygen added was 1/750th part of the whole. If we add

much more oxygen than this, the yellow glow begins to be spoilt, and 2 per cent. admixture destroys it altogether.

As I have explained, oxygen is not the only admixture that brings in the yellow glow again. Among gases that do not contain oxygen, hydrogen sulphide, ethylene, and methane will do the same. Methane acted when present in very small concentrations. It had a perceptible effect when only 1/30,000th part was added to the nitrogen stream.

I have seen a criticism of these experiments in which it is suggested that no sufficient precautions were taken to guard against traces of oxygen or oxygen compounds in these added gases. This criticism does not seem to be well considered. If, for instance, we supposed the "methane" (which, as a matter of fact, was carefully prepared from aluminium carbide and purified by liquefaction and fractional evaporation) to *consist entirely of pure oxygen*, the observed facts would not be covered, for the methane added in the experiment just cited was only about 1/10th of the minimum amount of oxygen required to produce an observable effect.

This action of foreign substances in encouraging the production of active nitrogen is very mysterious, although not perhaps more so than the necessity for minute traces of water in many commonplace chemical reactions, which has been so admirably established by my colleague, Prof. Baker. I was at one time hopeful of connecting it with a change in the conditions of the electric discharge, and it is true that the introduction of a trace of oxygen, for example, considerably increases the drop of potential over the cathode at the same time that it increases the yield of active nitrogen. On the other hand, we may arrange so that the stream of nitrogen gas does not reach the cathode, but is led away after being exposed to the positive part of the discharge only. In this case, we find that a trace of oxygen produces the usual favourable effect on the generation of active nitrogen without at all affecting the electrical conditions in that part of the discharge which is operative.

The whole of this part of the subject requires further study; and, in conclusion, I must admit that investigations, now lasting more than seven years, have only touched the fringe of the subject.

XXIV.—*Studies in the Phenylsuccinic Acid Series. Part VI. Racemisation Phenomena Observed during the Investigation of the Optically Active Phenyl- and Diphenyl-succinic Acids and their Derivatives.*

By Henry Wren.

It has been recently shown (Wren and Still, T., 1917, **111**, 1019) that the esters of *r*- and *meso*-diphenylsuccinic acids are interconvertible under the influence of alkali. To quote a specific example, ethyl *r*-diphenylsuccinate is almost quantitatively transformed into the ester of the *meso*-acid when its alcoholic solution is treated with a solution of sodium ethoxide in ethyl alcohol; also, when the ester is hydrolysed with an insufficient amount of aqueous ethyl-alcoholic potassium hydroxide solution, the non-hydrolysed portion is found to have suffered partial isomerisation, with the production of ethyl *meso*diphenylsuccinate. Since, in solution at any rate, ethyl *r*-diphenylsuccinate may be regarded as a molecular mixture of ethyl *d*-diphenylsuccinate and ethyl *l*-diphenylsuccinate, it was to be expected that the esters of the optically active acids would separately undergo similar transformation, and would therefore become racemised, the possibility of a balanced action being excluded in this case, since any further isomerisation of the *meso*-ester which might be formed would merely lead to the production of the *r*-ester. The theoretical expectations have been fully confirmed by a series of experiments with the methyl and ethyl esters of the optically active acids. A typical example is furnished by the formation of ethyl *meso*-diphenylsuccinate as a product of the action of ethyl-alcoholic sodium ethoxide on ethyl *l*-diphenylsuccinate. Similarly, when ethyl *d*-diphenylsuccinate is hydrolysed with an insufficient amount of aqueous ethyl-alcoholic potassium hydroxide solution, the non-hydrolysed portion is found to be almost inactive towards polarised light and to consist practically entirely of ethyl *meso*diphenylsuccinate. It would thus appear that the racemisation previously observed to occur during the hydrolysis of esters of the optically active diphenylsuccinic acids (Wren and Still, T., 1915, **107**, 1454) takes place in part, at any rate, previous to the actual hydrolysis, and is thus due to rearrangement of the ester, and not of the acid. The greater liability of esters as compared with the corresponding acids to racemisation under the influence of alcoholic alkali has been pointed out by Gadamer (*Chem. Zeit.*, 1910, **34**, 1004; *J. pr.*

Chem., 1913, [ii], **87**, 312), who found that, whilst the esters of tropic acid are readily racemised, the acid itself is not racemised by hydroxyl ions. This difference in behaviour is ascribed to the ionisation of the acid at the carboxyl group, whilst the ester, which behaves as a pseudo-acid, only becomes ionised in the presence of hydroxyl ions, thus:

$$\begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2H\end{matrix} \qquad\qquad \begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2R\end{matrix}$$

Tropic acid. Esters of tropic acid.

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$\begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2\end{matrix} \qquad\qquad \begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}\\CO_2R\end{matrix}$$

It has, however, been pointed out by Frankland (T., 1913, **103**, 725) that the racemisation may be due to loss of asymmetry caused by tautomeric change previous to ionisation, thus:

$$\begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}H\\CO_2R\end{matrix} \quad\longrightarrow\quad \begin{matrix}C_6H_5\\HO\cdot CH_2\end{matrix}\!>C:C<\!\begin{matrix}OH\\OR\end{matrix}$$

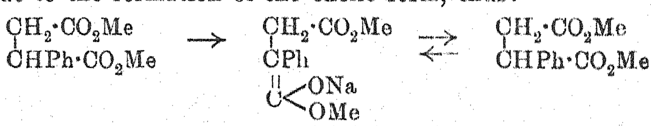
The only instance of racemisation of an ester previous to hydrolysis which appears to have been noted in the literature is the observation of McKenzie and Widdows (T., 1915, **107**, 713) that *l*-menthyl *d*-phenyl-*p*-tolylacetate is, in part, catalytically racemised by alkali prior to its undergoing hydrolysis. In a case which presents some analogies, Wren (T., 1909, **95**, 1596) found that the portion of the ester which escapes conversion into amide is partly inactivated when methyl *l*-mandelate is acted on by cold alcoholic ammonia.

The observations have been extended to the optically active phenylsuccinic acids and their esters, since the latter substances are much more readily soluble than the derivatives of the diphenylsuccinic acids, and therefore allow the course of racemisation to be followed directly by polarimetric measurement. It is thus found that ethyl and methyl *d*-phenylsuccinates are rapidly and completely racemised by the action of a solution of the requisite sodium alkyloxide in the corresponding alcohol, and also that when the latter ester is treated with potassium hydroxide dissolved in slightly aqueous ethyl alcohol in quantity insufficient for complete hydrolysis, the non-hydrolysed portion is almost completely racemised under the conditions described in the experimental section of the paper.

Some time ago, it was found by Wren and Williams (T., 1916, **109**, 579) that a partly racemised acid was obtained when methyl *d*-phenylsuccinate is hydrolysed by an excess of aqueous ethyl-

alcoholic potassium hydroxide solution. Thus, in one experiment, the ester was heated with about six times the theoretically necessary quantity of potassium hydroxide dissolved in aqueous ethyl alcohol (water: alcohol: :1 vol.: 2 vols.), when the recovered acid was found to have $[\alpha]_D + 110\cdot2°$ in acetone solution, whilst the parent acid had $[\alpha]_D^{12\cdot5} + 175\cdot4°$. The considerable activity of this acid became somewhat remarkable when considered in conjunction with the almost complete racemisation of the non-hydrolysed ester in the experiment just quoted, and pointed to a profound influence of the varying factors, namely, the amount of potassium hydroxide and the water content of the solution. The effect of variation in the latter was therefore studied, and was found to exercise a very marked influence on the optical activity of the recovered acid. In three strictly comparable experiments, in which the only differences consisted in the use of absolute, approximately 80 per cent. and 50 per cent. alcohol respectively, the acid formed by hydrolysis was found to have $[\alpha]_D + 3\cdot1°$, $+59\cdot1°$, and $+100\cdot3°$ respectively in ethyl-alcoholic solution in which the parent acid had $[\alpha]_D + 147\cdot4°$; under closely similar conditions, the latter acid was found to be unaffected by the action of an excess of alcoholic or aqueous-alcoholic sodium hydroxide solution.

During the last few years, a considerable amount of evidence has been accumulated which indicates that racemisation under the influence of alkali may frequently be attributed to keto-enolic desmotropy, with consequent disappearance of the asymmetry of the compound. In the present instance, the inactivation of methyl *d*-phenylsuccinate when acted on by sodium methoxide may be due to the formation of the enolic form, thus:



Active. Inactive. Inactive.

The evidence which has been brought forward in favour of such an explanation of racemisation in analogous case is, so far, of a purely qualitative nature; in no single instance has the enolic form been isolated or its amount determined. The actual separation of the enolic modification would doubtless be a matter of great difficulty in many cases, since the proportion of enolised molecules need be but infinitesimal to account for the phenomena of racemisation. On the other hand, it was hoped to be able to bring quantitative evidence of the presence of the enolic modification by utilising the method adopted by K. H. Meyer (*Ber.*, 1912, **45**, 2864) in his investigations on ethyl malonate and ethyl

methanetricarboxylate. Direct titration of a methyl-alcoholic solution of methyl *d*- or *r*-phenylsuccinate with bromine failed to disclose the presence of any enol, and a similar result was obtained when experiments were performed on the esters dissolved in methyl-alcoholic sodium methoxide solution, although under the latter conditions ethyl malonate was found to be largely enolised. The experimental conditions were not greatly varied in this case, however, since the objection could possibly be raised that, in order to demonstrate the point at issue, it would be necessary to show definitely that enolisation occurs in such a manner as to form compound I, and not II:

$$\begin{array}{l} CH_2\cdot CO_2Me \\ \vert \\ CPh \\ \Vert \\ C\Big\langle\begin{array}{l}ONa\\OMe\end{array} \\ \quad (I.) \end{array} \qquad\qquad \begin{array}{l} C\Big\langle\begin{array}{l}OMe\\ONa\end{array} \\ \Vert \\ CH \\ \vert \\ CHPh\cdot CO_2Me \\ \quad (II.) \end{array}$$

It is hoped to apply the method, however, to esters of certain monobasic acids to which this objection cannot be urged.

Lastly, if racemisation be attributable to the formation of an enolic derivative, it would be expected that the nature of the basic atom or group of the alkali would have an influence on the result. Experiments on the hydrolysis of methyl *d*-phenylsuccinate with aqueous ethyl-alcoholic tetramethylammonium hydroxide solution were therefore performed; racemisation was found to be even more pronounced than with potassium hydroxide solution under nearly similar conditions.

EXPERIMENTAL.

Formation of Ethyl meso*Diphenylsuccinate from Ethyl* d- *and* l-*Diphenylsuccinates.*

A. *By the Action of Ethyl-alcoholic Sodium Ethoxide Solution.*—Ethyl *l*-diphenylsuccinate (1 gram) was warmed with a solution of sodium ethoxide in ethyl alcohol (0·666*N*; 20 c.c.) in a closed vessel to about 50°, when it dissolved completely; the solution was allowed to cool to the ordinary temperature, when it became almost solid. After remaining during three days at the temperature of the laboratory, the precipitate was removed and washed successively with alcohol, warm water, and, finally, alcohol. It melted at 139—140°, and was optically inactive in acetone solution. After being crystallised from rectified spirit, ethyl *meso*diphenylsuccinate was obtained in well-defined needles melting at 140—141°.

B. *By Partial Hydrolysis.*—Ethyl *d*-diphenylsuccinate (1·5

grams) was heated during four hours with aqueous ethyl-alcoholic potassium hydroxide solution ($0{\cdot}25N$; 15 c.c.), this being about three-fifths of the quantity required for complete hydrolysis. The solution was diluted with water, and the unattacked esters were extracted with chloroform. The residue, obtained after removal of the latter, melted at 138—140°; it had $[\alpha]_D$ +5·4° in acetone solution ($l=2$, $c=1{\cdot}113$, $\alpha_D+0{\cdot}12°$), whereas the pure *d*-ester has $[\alpha]_D^{16}$ +279·4° under similar conditions. After being crystallised from rectified spirit, it yielded pure ethyl *meso*diphenylsuccinate, which was optically inactive in acetone solution and melted at 140—141°.

Formation of Methyl meso*Diphenylsuccinate from Methyl* l- *and* d-*Diphenylsuccinates.*

A. *By the Action of a Methyl-alcoholic Solution of Sodium Methoxide.*—Methyl *l*-diphenylsuccinate (1 gram) was heated in a stoppered flask during four hours at 55—65° with a solution of sodium methoxide in absolute methyl alcohol ($0{\cdot}704N$; 60 c.c.). When the solution was cooled, a quantity of fine, prismatic crystals separated, which were removed, washed with water and methyl alcohol, and dried. After being crystallised from acetone, the product was obtained in well-defined needles, which were optically inactive when dissolved in chloroform ($l=2$, $c=0{\cdot}5115$), and were identified as methyl *meso*diphenylsuccinate by their crystalline form, melting point (218·5—219·5°) alone, and when mixed with an approximately equal quantity of the synthetic *meso*-ester.

B. *By Partial Hydrolysis.*—A solution of methyl *l*-diphenylsuccinate (1·5 grams) in boiling methyl alcohol (100 c.c.) was heated during four hours with aqueous methyl-alcoholic potassium hydroxide solution ($0{\cdot}593N$; 8 c.c.), this being approximately half the quantity of alkali required for the complete hydrolysis of this amount of the ester. The alcohol was removed on the water-bath and the residue warmed with water. The undissolved portion was removed and dried. It was optically inactive when dissolved in chloroform ($l=2$, $c=0{\cdot}8365$), and, after being crystallised from acetone, yielded methyl *meso*diphenylsuccinate, which melted at 218·5—219·5°; the melting point was unaltered by admixture with the synthetic *meso*-ester.

Racemisation of Methyl and Ethyl d-*Phenylsuccinates under the Influence of Alkali.*

A. *By Sodium Alkyloxide.*—Methyl *d*-phenylsuccinate (0·8157 gram) was dissolved in methyl-alcoholic sodium methoxide solution (20·5 c.c.), and transferred as rapidly as possible to a 2-dcm. tube. Approximately three minutes after being prepared, the solution had α_D +8°, but the field was somewhat cloudy, and the activity altered too rapidly to allow of accurate measurement. After about fifteen minutes, the value had decreased to +3·5°, after forty minutes to +0·5°, after seventy minutes to +0·17°, after one hundred minutes to +0·05°. After two hours, the solution was poured into a slight excess of dilute hydrochloric acid. The ester was extracted with ether, the ethereal solution washed with sodium carbonate, and dried over calcium chloride. The residue, obtained after removal of the solvent, solidified readily, and was optically inactive in acetone solution ($l=2$, $c=1·555$). After being crystallised from light petroleum, it yielded characteristic clusters of prisms of methyl *r*-phenylsuccinate, which melted at 57·5—58·5°. The melting point remained unchanged when the substance was mixed with the synthetic *r*-ester.

In a similar manner, ethyl *d*-phenylsuccinate (0·9964 gram) was dissolved in ethyl-alcoholic sodium ethoxide solution (1·059*N*; 20 c.c.). In this case, racemisation proceeded so rapidly as to be almost complete before polarimetric measurements could be made, and the solution had become quite inactive within ten minutes. Since the liquid nature of the ethyl *r*-ester rendered the identification of a small quantity of it a matter of difficulty, water was added to the solution, and the ester hydrolysed. The resulting *r*-phenylsuccinic acid melted at 167—168°, whereas Higson and Thorpe (T., 1906, **89**, 1470) give 168° as the melting point of this acid.

B. *By Partial Hydrolysis.*—Methyl *d*-phenylsuccinate (3 grams) was heated to boiling during two and a-half hours with slightly aqueous methyl-alcoholic potassium hydroxide solution (0·395*N*; 25 c.c.), this being rather more than one-third of the quantity theoretically necessary for complete hydrolysis. The alcohol was removed on the water-bath, and the residue mixed with water and shaken with ether. The residue (about 0·3 gram) obtained after removal of the ether solidified readily, and had $[\alpha]_D$ +2·12° when dissolved in acetone ($l=2$, $c=1·178$, α_D +0·05°), whereas the pure ester has $[\alpha]_D^{10}$ +152·2° under similar conditions. After being crystallised from light petroleum (b. p. 40—60°), it yielded pure

methyl *r*-phenylsuccinate, which melted at 57—58·5°; this value remained unchanged after admixture with the synthetic ester.

Action of Alkali on l-*Phenylsuccinic Acid.*

The *l*-phenylsuccinic acid used in these experiments had $[\alpha]_D$ −148·3° in ethyl-alcoholic solution, a value which agrees well with the data of Wren and Williams (*loc. cit.*).

Three comparative experiments were performed, in which the acid (1 gram) was treated in a closed vessel with (*a*) sodium ethoxide solution (1·059*N*; 50 c.c.) and absolute ethyl alcohol (20 c.c.); (*b*) sodium ethoxide solution (50 c.c.), alcohol (20 c.c.), and water (0·95 c.c.), and (*c*) sodium ethoxide solution (50 c.c.), alcohol (10 c.c.), and water (10 c.c.). In each case a certain amount of precipitate separated. The mixtures were heated with frequent agitation during five hours at 70°, then neutralised with hydrochloric acid, and evaporated to remove alcohol; the acids were isolated by extraction of the acidified solutions with ether. The dried acids were polarimetrically examined in ethyl-alcoholic solution, the values for the specific rotations being (*a*) −146·6° ($l=2$, $c=2·8815$, α_D −8·45°), (*b*) −145·5° ($l=2$, $c=1·691$, α_D −4·92°), and (*c*) −146·2° ($l=2$, $c=1·7035$, α_D −4·98°). In no case, therefore, was any evidence of racemisation obtained.

Complete Hydrolysis of Methyl d-*Phenylsuccinate by Alcoholic Sodium Hydroxide containing differing Proportions of Water.*

In these experiments, the weight of ester and alkali, the total volume of the solution, the temperature, and duration were maintained uniform, the only variation consisting in the replacement of differing volumes of alcohol by water. Stock solutions of ester were prepared by dissolving 2 grams of the latter in 30 c.c. of ethyl alcohol, and of alkali by dissolving sodium in absolute ethyl alcohol; the latter solution was 1·1*N*. Ten c.c. of the ester solution were mixed with (*a*) alkali solution (25 c.c.), alcohol (25 c.c.), and water (0·45 c.c.); (*b*) alkali solution (25 c.c.), alcohol (15 c.c.), water (10 c.c.), and (*c*) alkali solution (25 c.c.), water (25 c.c.). The solutions were heated in closed flasks during four hours at 60—65°; precipitates speedily separated in (*a*) and (*b*) but (*c*) remained homogeneous throughout. The resulting mixtures were nearly neutralised with hydrochloric acid and evaporated to remove alcohol; the aqueous solutions were extracted with ether after acidification with mineral acid. The residual phenylsuccinic acids were polarimetrically examined in ethyl-alcoholic solution, when

the following values were observed for the specific rotation: (*a*) $+3{\cdot}1^\circ$ ($l=2$, $c=2{\cdot}2391$, α_D $+0{\cdot}14^\circ$); (*b*) $+59{\cdot}1^\circ$ ($l=2$, $c=1{\cdot}913$, α_D $+2{\cdot}26^\circ$); (*c*) $+100{\cdot}3^\circ$ ($l=2$, $c=2{\cdot}0731$, α_D $+4{\cdot}16^\circ$).

Complete Hydrolysis of Methyl d-*Phenylsuccinate by Aqueous-Alcoholic Tetramethylammonium Hydroxide Solution.*

The solution of the alkali was prepared by warming an aqueous solution of tetramethylammonium iodide with a slight excess of silver oxide, and removal of silver iodide and unchanged oxide. The filtrate was concentrated to 14 c.c., and then diluted with ethyl alcohol to 55 c.c. An approximately *N*-solution was thus obtained.

The methyl *d*-ester (1 gram) was heated during two and a-half hours with the solution described above, and the corresponding acid isolated in the usual manner; it melted at 164—168·5°, and had $[\alpha]_D$ $+10{\cdot}1^\circ$ in ethyl-alcoholic solution ($l=2$, $c=3{\cdot}329$, α_D $+0{\cdot}67^\circ$).

Action of Ferric Chloride on Methyl d-*Phenylsuccinate.*

It has been shown by Meyer (*Ber.*, 1911, **44**, 2725) in the case of ethyl acetoacetate that ferric chloride exerts a direct enolising action. The behaviour of an ethyl-alcoholic solution of methyl *d*-phenylsuccinate towards anhydrous ferric chloride has therefore been polarimetrically investigated in the expectation that enolisation, if induced at the asymmetric carbon atom, would betray itself by racemisation. The solutions, however, were found to be optically stable under these conditions.

Methyl *d*-phenylsuccinate (0·4869 gram) was dissolved in ethyl alcohol and the solution made up to 20 c.c.; a portion of this solution had α_D $+6{\cdot}73^\circ$ when examined in a 2-dcm. tube, and this value had not changed at the end of forty hours after the addition of a small quantity of ferric chloride. A further portion of the latter substance was added, and the solution allowed to remain at the temperature of the laboratory during nine days, at the end of which period the ester was isolated and examined in ethyl-alcoholic solution; it had $[\alpha]_D$ $+129{\cdot}8^\circ$, whereas the value $+138{\cdot}2^\circ$ had been determined for the original specimen.

Possible Enolisation of Methyl Phenylsuccinate in Solution.

Methyl *d*-phenylsuccinate (0·5369 gram) and methyl *r*-phenylsuccinate (0·4496 gram) were separately dissolved in methyl alcohol

(20 c.c.) and titrated with an $N/10$-solution of bromine in the same solvent until a faint, permanent, yellow coloration was produced; 0·55 c.c. of bromine was required in each case, whilst in a blank experiment 0·60 c.c. was necessary.

Methyl *d*-phenylsuccinate (0·3292 gram) was dissolved in a well-cooled methyl-alcoholic solution of sodium methoxide, and the product poured into an excess of a solution of bromine in methyl alcohol containing hydrogen chloride. Excess of bromine was removed by the addition of β-naphthol dissolved in methyl alcohol, and the resulting solution warmed after addition of aqueous potassium iodide (10 per cent.). The liberated iodine required 0·3 c.c. of $N/10$-sodium thiosulphate solution, this quantity being the same as that required in a blank experiment.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed a part of the cost of the investigation.

MUNICIPAL TECHNICAL INSTITUTE,
BELFAST.
[*Received, February 20th*, 1918.]

XXV.—*Synthesis of 3:4-Dihydroxyphenanthrene (Morphol) and of 3:4-Phenanthraquinone.*

By GEORGE BARGER.

Two years ago a note was published (T., 1916, **109**, 568) describing the preparation of 3-phenanthrol-4-aldehyde, first carried out at my suggestion by a former pupil, the late J. W. Smith. As there indicated, I was able to deduce the constitution of the aldehyde from its conversion into 3:4-dihydroxyphenanthrene (morphol). From this, 3:4-phenanthraquinone was subsequently obtained, and since there has been no opportunity of further experiment in this direction, the preparation of these two compounds is described below. Morphol had not yet been synthesised, and was only known as a degradation product of morphine, for although Pschorr and Simuleanu (*Ber.*, 1900, **33**, 1810) prepared its dimethyl ether by Pschorr's well-known general method, they were unable to demethylate this compound without reduction; on boiling with hydriodic acid they only obtained 3-phenanthrol.

EXPERIMENTAL.

3:4-*Dihydroxyphenanthrene* (Morphol).

Ortho- and para-hydroxyaldehydes may be converted, often quantitatively, into the corresponding diphenols by a reaction due to Dakin (P., 1909, **25**, 194; *Amer. Chem. J.*, 1909, **42**, 477). In spite of its convenience and wide applicability, this reaction has, strangely enough, received very little attention. Dakin dissolves the aldehyde in one equivalent of sodium hydroxide and adds a molecular proportion of dilute hydrogen peroxide, when oxidation takes place at once with distinct evolution of heat. On applying the reaction to 3-phenanthrolaldehyde, the sparing solubility of the sodium salt made it necessary to work in very dilute solution, and only a minute quantity of the diphenanthrol was at first obtained. This difficulty was readily overcome by working in pyridine solution and limiting the amount of water as far as possible by the use of highly concentrated potassium hydroxide and hydrogen peroxide, as follows.

3-Phenanthrolaldehyde (1·11 grams) was dissolved in pyridine (10 c.c.) in a flask provided with a dropping funnel and exit tube, and after the air had been displaced by hydrogen, 0·55 c.c. of 30·8 per cent. hydrogen peroxide and then 0·45 c.c. of 12·5 *N*-potassium hydroxide were added through the tap funnel, which was washed out by a few drops of water. The addition of the potassium hydroxide caused a considerable rise in temperature (but hydrogen peroxide alone, with pyridine, does not react). After boiling for a few seconds, the solution was cooled and excess of hydrochloric acid was added through the funnel. The solution was then extracted with ether, and the ethereal extract washed free from pyridine with acid. On evaporation of the ether, the dihydroxyphenanthrene crystallised; the yield of the crude product was 1·05 grams. It was dissolved in 5 c.c. of boiling benzene, when, on cooling, 0·61 gram separated in almost colourless crystals, and a further 0·22 gram was obtained by adding light petroleum to the mother liquor, the total yield of pure substance thus amounting to 80 per cent. of the theoretical. The substance so obtained was very sensitive to oxidation; it instantly reduced silver nitrate in neutral solution at the ordinary temperature. A trace of ferric chloride gave a reddish-brown coloration, but excess caused oxidation. It was recrystallised from water and from petroleum, b. p. 80—90°, and then melted at 142—143°, so that it seemed to be identical with morphol (O. Fischer and Vongerichten, *Ber.*, 1886, **19**, 793, give 143°). By recrystallisation, it was obtained almost,

but not quite colourless. A perfectly colourless specimen resulted on sublimation in the vacuum of a Gaede pump at 130°, but the sublimate melted at 142°. On acetylation by boiling with acetic anhydride and a trace of sulphuric acid, an acetyl compound was obtained, which, after crystallisation from petroleum, b. p. 80—90°, and then from methyl alcohol, melted at 158° (O. Fischer and Vongerichten give 159° as the melting point of diacetylmorphol).

Since no morphol was available for direct comparison, the diphenol was methylated in order to provide a conclusive proof of its identity, for both the possible dimethyl ethers, 2:3- and 3:4-dimethoxyphenanthrene, have been synthesised by Pschorr and his pupils.

The crude oxidation product from 1·11 grams of the hydroxyaldehyde was dissolved in 10 c.c. of methyl alcohol and 0·85 c.c. of methyl sulphate (2 molecular proportions), and 0·72 c.c. of 12·5*N*-potassium hydroxide were added alternately four times. After adding ether, washing with sodium hydroxide, drying, and evaporating the ether, the residue was distilled twice under 12 mm. pressure. At first, crystallisation could not be induced, but a trace crystallised from methyl alcohol on spontaneous evaporation of the solvent, and on adding this to the main bulk, the whole solidified almost completely. The crystals were drained on a tile, the yield was 0·3 gram. When recrystallised from methyl alcohol by evaporation at the ordinary temperature, narrow, rectangular plates were obtained melting at 45°. The picrate formed ruby-red crystals melting at 105—106°, and the dibromo-derivative colourless needles melting at 124—125°. The melting points of 3:4-dimethoxyphenanthrene, its picrate, and its dibromo-derivative are given by Pschorr and Simuleanu (*Ber.*, 1900, **33**, 1810) as 44°, 105—106°, and 124—125° respectively, and those of the corresponding 2:3-derivatives by Pschorr and Buckow (*Ber.*, 1900, **33**, 1829) as 131°, 127—128°, and 160° respectively, so that the diphenol is identified with certainty as 3:4-dihydroxyphenanthrene and the aldehyde, from which it is derived, as 3-phenanthrol-4-aldehyde.

3:4-*Phenanthraquinone*, $C_{14}H_8O_2$

Having found a comparatively ready method of preparing morphol, I was able to oxidise it to the corresponding quinone by Willstätter and Pfannenstiehl's method (*Ber.*, 1904, **37**, 4744). Five grams of silver nitrate were decomposed in a stoppered cylinder with the calculated quantity of sodium hydroxide, and the silver oxide was washed by decantation twelve times with water, six

times with acetone, and six times with dry ether. Then an ethereal solution of 0·8 gram of morphol was added, together with 2 grams of anhydrous sodium sulphate, and the mixture was shaken for fifteen seconds. A blood-red solution was formed at once, and, after settling, was decanted; the silver oxide was extracted repeatedly with ether until the solvent was no longer coloured red. On evaporation, the quinone crystallised. It was dissolved in 25 c.c. of boiling benzene, when, on cooling, 0·52 gram separated, or 65 per cent. of the theoretical. A little more was obtained by concentrating the mother liquor and adding light petroleum. 3:4-*Phenanthraquinone* was thus obtained in brilliant red, short, pointed prisms. The melting point is not sharp; at 125—130° the substance blackens, and on rapid heating melts in the neighbourhood of 132—133°:

0·1412 (dried at 100°) gave 0·4167 CO_2 and 0·0501 H_2O. C=80·5; H=3·9.

$C_{14}H_8O_2$ requires C=80·8; H=3·9 per cent.

The substance is a true derivative of *o*-benzoquinone, resembling 1:2-naphthaquinone rather than 9:10-phenanthraquinone in colour and instability. It further differs from 9:10-phenanthraquinone in not yielding Laubenheimer's reaction.

It is at once reduced by sulphurous acid to morphol. In the oxidation of the latter with silver oxide, no isomeric colourless form of the quinone could be observed, as in the case of *o*-benzoquinone (Willstätter and Müller, *Ber.*, 1908, **41**, 2580). It was easy to repeat their experiments with catechol, but not with morphol.

The phenanthrene employed in making the above substances was purchased with a grant from the Research Fund of the Chemical Society, for which grateful acknowledgment is made.

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XXVI.—*The Alkaloids of Ipecacuanha. Part III.*

By FRANK LEE PYMAN.

IN the previous paper of this series (T., 1917, **111**, 424), it was shown that *O*-methylpsychotrine gave a mixture containing emetine and *iso*emetine* on reduction. The formation of *iso*emetine was demonstrated by the isolation of its benzoyl derivative, for neither *iso*emetine nor any of its salts had at that time been obtained in a crystalline form. Later, however, the *hydrobromide* became crystalline, and was readily purified by crystallisation from water, and, from the pure salt, the *base*, *hydrochloride*, and *hydrogen oxalate* were prepared in the usual manner, and also obtained in crystalline form. On benzoylation, the base gave the benzoyl*iso*emetine previously described. Since emetine and *iso*emetine are produced by the reduction of methylpsychotrine, it was to be expected that *iso*emetine, like emetine, could be oxidised to methylpsychotrine and rubremetine, and this proved to be the case. The view that emetine and *iso*emetine are stereoisomerides was thus confirmed, and it appeared to be of interest to determine whether an equilibrium between the two bases could be established by boiling with amyl alcohol and sodium amyloxide. Experiments to this end were unsuccessful, for, after fourteen hours' boiling, no evidence of partial racemisation was obtained, each base being recovered unchanged except in so far as it had been hydrolysed to phenolic bases.

The fact that psychotrine gives cephaeline and *iso*cephaeline on reduction, whilst the methyl ether of psychotrine gives emetine and *iso*emetine, indicated the probability that *iso*emetine was the methyl ether of *iso*cephaeline, and this has now been proved by preparing *iso*emetine by the methylation of *iso*cephaeline.

When methylated under suitable conditions, *iso*emetine gives a well-crystallised *N*-methyl derivative, N-*methyl*iso*emetine*, which proves to be the *O*-methyl ether of the isomeride of *N*-methylcephaeline previously described (T., 1914, **105**, 1624); this substance is therefore N-*methyl*iso*cephaeline*.

* The term *iso*emetine is clearly appropriate to this compound, which is the methyl ether of the *iso*cephaeline described in 1914 (Carr and Pyman, T., 1914, **105**, 1591), and the parent of the substance already named benzoyl*iso*emetine (Pyman, T., 1917, **111**, 424). It has since been employed by Karrer (*Ber.*, 1917, **50**, 582) for a reduction product of rubremetine. Whilst the coincidence is unfortunate, it does not appear to be important, for Karrer's '*iso*emetine'—an amorphous base from which no crystalline derivatives were prepared—is probably a mixture of stereoisomerides.

Complete methylation of *iso*emetine yields a well-crystallised N-*methyl*iso*emetine methiodide*, which is accompanied by an amorphous salt. This is probably a mixture of the two stereoisomeric methiodides of *N*-methyl*iso*emetine, the isomerism of which depends on the presence of an asymmetric nitrogen atom, for it is shown later that the complete methylation of emetine leads to a similar result. This view is borne out by the fact that the crystalline and amorphous salts give N-*methyl*iso*emetinemethine* in equally good yield when converted into the corresponding methohydroxides and evaporated in a vacuum. This methine, like that of emetine, crystallises well as the neutral *oxalate*, and also forms a well-crystallised *methiodide*. So far, attempts to effect its further degradation have not led to crystalline products.

The connexion between the compounds described above and their relation to the compounds described in the previous papers is shown in the diagram on p. 225.

Reference has been made above to the formation of two stereoisomeric methiodides by the complete methylation of emetine. This operation, which consists in heating emetine with methyl iodide and aqueous sodium carbonate, has been carried out previously by several authors, but hitherto only one methiodide has been isolated, although the formation of "by-products" has been observed. In view of the fact that emetine contains a tertiary nitrogen atom common to two ring complexes, the formation of two stereoisomeric *N*-methylemetine methiodides owing their separate existence to the asymmetry of this nitrogen atom appeared to be possible. On experiment, it was found that the product of the reaction gave, besides the previously known methiodide, which melts at 225—226° (corr.) and has $[\alpha]_D$ $-10°$, a stereoisomeride, which melts at 262° (corr.) and has $[\alpha]_D$ $+68°$. Proof that this is, in fact, a stereoisomeric *N*-methylemetine methiodide, and not a derivative of some impurity in the emetine employed, is afforded by the fact that it yields the same methine as does the previously known methiodide. In accordance with the usual practice (compare Scholtz, *Ber.*, 1905, **38**, 595; Voss and Gadamer, *Arch. Pharm.*, 1910, **248**, 43; Jowett and Pyman, T., 1913, **103**, 290), the salt of lower melting point is termed the α-salt, that of higher melting point the β-salt. In previous cases, it has been possible to convert the α-salt into the β-salt by heating it above its melting point. α-*N*-Methylemetine methiodide, however, effervesces at its melting point and probably undergoes decomposition, for none of the β-salt could be isolated from the reaction product.

The remarkable influence of stereochemical structure on physiological action, which has been observed in many other cases, is

apparent in the case of emetine and *iso*emetine, which differ only in the sign of one asymmetric carbon atom.

Dr. H. H. Dale, F.R.S., of the staff of the Medical Research Committee, has kindly determined the relative toxicity of these compounds, and finds that *iso*emetine is rather less than half as toxic as emetine. The results of intravenous administration of different doses of their hydrochlorides to rabbits were as follows:

Emetine hydrochloride.		*iso*Emetine *hydrochloride.*	
4·25 mgm.* per kilo.	—All died.	9·0 mgm.* per kilo.	—All died.
4·0 ,, ,,	—4 died out of 5.	8·5 ,, ,,	—4 died out of 6.
3·75 ,, ,,	—1 died out of 4.	8·25 ,, ,,	—3 died out of 6.
3·5 or less ,,	—All lived.	8·0 ,, ,,	—1 died out of 4.
		7·5 or less ,,	—All lived.

* Of the anhydrous salt.

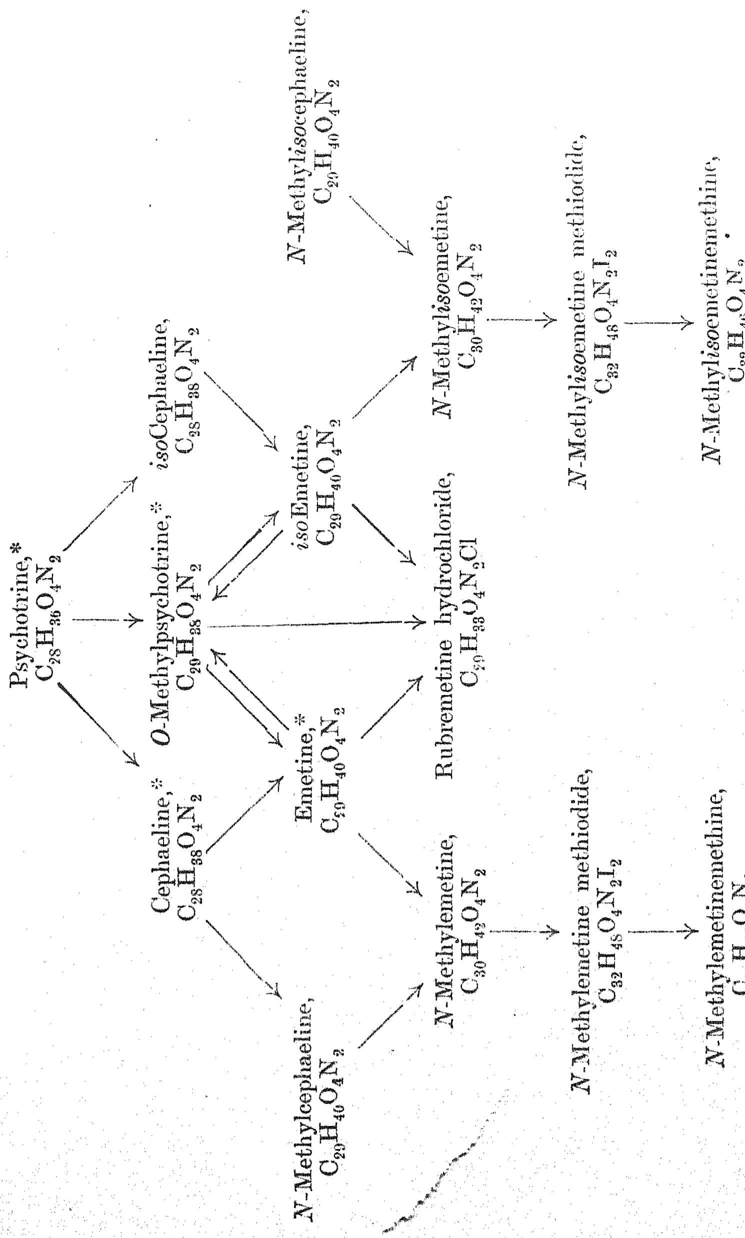
With both compounds, death resulted from acute heart failure. It was also found that *iso*emetine was practically non-emetic for cats.

A clinical trial of *iso*emetine has been carried out by Dr. G. C. Low, to whom the author's thanks are due. Whilst emetine given in amœbic dysentery nauseates the patient, but brings about the elimination of the amœbæ, Dr. Low finds that *iso*emetine is well tolerated in comparatively large doses, but does not appear to have any effect on the amœbæ.

EXPERIMENTAL.

Isolation of iso*Emetine.*

*iso*Emetine occurs together with emetine and base "C" amongst the reduction products of methylpsychotrine. In order to isolate it, the syrupy base recovered from the mother liquors of emetine hydrobromide (T., 1917, **111**, 439, line 10) is dissolved in alcohol (2 parts) and mixed with a solution of hydrated oxalic acid (0·5 part) in alcohol (5 parts), and kept for several days, when a spongy, crystalline mass slowly separates. This is collected and washed with alcohol, when crude *iso*emetine hydrogen oxalate remains. Further quantities remain in the mother liquors from the crystallisation of the hydrogen oxalate of base "C" (*ibid.*, p. 438). The crude hydrogen oxalate is dissolved in water, and the base regenerated into ether by sodium hydroxide; after removing the solvent, the residue is dissolved in a slight excess of dilute hydrobromic acid, digested with animal charcoal, and filtered, when *iso*emetine hydrobromide separates on inoculating and cooling, and is purified readily by recrystallisation from water.



* Occurs naturally.

iso*Emetine*, $C_{29}H_{40}O_4N_2$.

The base crystallises from ether in characteristic disks (circular plates) formed of radiating needles, containing $1H_2O$, which is not completely lost in a vacuum. The air-dried base softens at 92° and melts at 97—98° (corr.); the same form and melting point were observed after recrystallisation of the base from ethyl acetate.

Found, in air-dried base (from ether): C = 69·7; H = 8·5; loss in a vacuum = 2·5.

$C_{29}H_{40}O_4N_2,H_2O$ (498·5) requires C = 69·9; H = 8·5; loss of $1H_2O$ = 3·6 per cent.

The base is insoluble in water, but easily soluble in the usual organic solvents with the exception of light petroleum. Its colour-reactions with Fröhde's reagent (green) and sodium diazobenzene-*p*-sulphonate (red in the presence of sodium carbonate, little changed on the addition of dilute hydrochloric acid) are identical with those given by emetine.

The specific rotatory power of the base, dried in a vacuum, was determined in chloroform solution:

$$\alpha_D - 3{\cdot}33°;\ c = 3{\cdot}514;\ l = 2\text{-dcm.};\ [\alpha]_D - 47{\cdot}4°.$$

The *hydrochloride* was obtained as a mass of small needles by neutralising the base with aqueous hydrochloric acid, evaporating the solution to dryness, and boiling the residue with absolute alcohol. It melts and decomposes at 310° (corr.), and is easily soluble in water, but almost insoluble in absolute alcohol.

This salt is almost anhydrous, losing only 0·5 per cent. at 100°.

Found in dried salt: C = 62·6; H = 7·7; Cl = 12·8.

$C_{29}H_{40}O_4N_2,2HCl$ (553·4) requires C = 62·9; H = 7·7; Cl = 12·8 per cent.

The specific rotatory power of this salt was determined in aqueous solution, and found to be negative at high, but positive at low concentrations:

$$\alpha_D - 4{\cdot}70°;\ c = 15{\cdot}07;\ l = 2\text{-dcm.};\ [\alpha]_D - 15{\cdot}6°.$$
$$\alpha_D - 0{\cdot}87°;\ c = 8{\cdot}134;\ l = 2\text{-dcm.};\ [\alpha]_D - 5{\cdot}3°.$$
$$\alpha_D + 0{\cdot}38°;\ c = 4{\cdot}092;\ l = 2\text{-dcm.};\ [\alpha]_D + 4{\cdot}6°.$$
$$\alpha_D + 0{\cdot}35°;\ c = 2{\cdot}259;\ l = 2\text{-dcm.};\ [\alpha]_D + 7{\cdot}7°.$$
$$\alpha_D + 0{\cdot}23°;\ c = 0{\cdot}909;\ l = 2\text{-dcm.};\ [\alpha]_D + 12{\cdot}7°.$$

The *hydrobromide* crystallises from water in well-formed prisms, which contain $4H_2O$. It is easily soluble in hot, but sparingly so (1—2 per cent.) in cold water. After drying in a vacuum, it softens from 215° and gradually becomes transparent without flowing, up to 220° (corr.).

Found, in air-dried salt: C=48·8; H=7·2; loss in a vacuum, 10·1, 10·0, 10·0.

$C_{29}H_{40}O_4N_2,2HBr,4H_2O$ (714·4) requires C=48·7; H=7·1; H_2O=10·1 per cent.

Found, in dried salt: C=54·0, 54·4; H=6·7, 6·8; Br=24·7.

$C_{29}H_{40}O_4N_2,2HBr$ (642·3) requires C=54·2; H=6·6; Br=24·9 per cent.

The specific rotatory power of the hydrated salt was determined in aqueous solution:

$\alpha_D + 0·54°$; $c = 4·153$; $l = 2$-dcm.; $[\alpha]_D + 6·5°$.
$\alpha_D + 0·42°$; $c = 1·989$; $l = 2$-dcm.; $[\alpha]_D + 10·5°$.

The *hydrogen oxalate* crystallises from water in colourless prisms, which contain $5H_2O$, and melt at 92—95° (corr.). After drying at 100°, it has no definite melting point, but softens from about 150° and effervesces at about 165° (corr.). It is easily soluble in water or alcohol, but its solution in the latter deposits a colourless, spongy mass on keeping.

Found, in air-dried salt: loss in a vacuum=11·8.

$C_{29}H_{40}O_4N_2,2C_2H_2O_4,5H_2O$ (750·6) requires H_2O=12·0 per cent.

Found, in salt dried in a vacuum: C=59·8, 60·1; H=7·0, 6·8.

$C_{29}H_{40}O_4N_2,2C_2H_2O_4$ (660·5) requires C=60·0; H=6·7 per cent.

The specific rotatory power was determined in aqueous solution:

$\alpha_D + 0·25°$; $c = 8·019$; $l = 2$-dcm.; $[\alpha]_D + 1·6°$.
$\alpha_D + 0·50°$; $c = 3·856$; $l = 2$-dcm.; $[\alpha]_D + 6·5°$.
$\alpha_D + 0·50°$; $c = 2·958$; $l = 2$-dcm.; $[\alpha]_D + 8·5°$.
$\alpha_D + 0·33°$; $c = 1·454$; $l = 2$-dcm.; $[\alpha]_D + 11·3°$.

Methylation of iso*Cephaeline. Formation of* iso*Emetine.*

0·4 Gram of *iso*cephaeline (T., 1914, **105**, 1626) was dissolved in a solution of 0·05 gram of sodium in 35 c.c. of fusel oil boiling at 130—133°; 0·2 gram of anhydrous sodium methyl sulphate was added, and the mixture boiled for one and a-half hours under a reflux condenser. After acidifying with hydrochloric acid, the liquor was distilled with steam to remove the fusel oil, and the alkaloids were then regenerated to ether by means of sodium carbonate. The ethereal solution was extracted with dilute aqueous sodium hydroxide, which removed 0·15 gram of unchanged *iso*-cephaeline, evaporated to dryness, and converted into the hydrobromide, when 0·17 gram of crude *iso*emetine hydrobromide was obtained. After recrystallisation from water, this salt formed prismatic needles, having the melting point previously recorded, either alone or mixed with *iso*emetine hydrobromide resulting from

the reduction of methylpsychotrine. For further identification, the base was regenerated from the hydrobromide, when it crystallised from ether in the characteristic disks, melting at 97—98° (corr.), both alone and when mixed with a specimen of the base resulting from the reduction of methylpsychotrine.

Methylation of iso*Emetine. Formation of* N-*Methyl*iso*emetine and Isolation of Benzoyl*iso*emetine.*

*iso*Emetine was methylated by methyl sulphate and sodium methoxide, the resulting mixture of *N*-methyl*iso*emetine and unchanged *iso*emetine being separated by removing the latter as the benzoyl derivative, the hydrochloride of which can be extracted from aqueous solution by chloroform. The method is precisely similar to that employed for the methylation of emetine (T., 1914, **105**, 1617), to which reference may be made for further details.

*iso*Emetine, regenerated from 7·2 grams of the hydrated hydrobromide, was dissolved in a solution of 0·5 gram of sodium in 25 c.c. of methyl alcohol and treated with 2·5 grams of methyl sulphate, when 1·3 grams of *N*-methyl*iso*emetine and 2·1 grams of benzoyl*iso*emetine were obtained.

N-*Methyl*iso*emetine* crystallises from ether in clear, colourless, square tablets with bevelled edges. It melts at 152—153° (corr.), and crystallises again on cooling. It suffers no loss in a vacuum.

Found: C=72·8; H=8·5.

$C_{30}H_{42}O_4N_2$ (494·5) requires C=72·9; H=8·6 per cent.

The specific rotatory power was determined in chloroform solution:

$$\alpha_D - 2{\cdot}55°;\ c = 2{\cdot}550;\ l = 2\text{-dcm.};\ [\alpha]_D - 50{\cdot}0°.$$

Benzoyl*iso*emetine proved to be identical with the substance previously described under this name (T., 1917, **111**, 439). It formed colourless prismatic needles from acetone, which melted at 207—208° (corr.) alone or when mixed with the preparation to which reference has been made. The specific rotatory power in chloroform solution was found to be $[\alpha]_D + 47{\cdot}3°$ ($c = 2{\cdot}833$).

Methylation of N-*Methyl*iso*cephaeline. Formation of* N-*Methyl*iso*emetine.*

The isomeride (T., 1914, **107**, 1624) of *N*-methylcephaeline yields *N*-methyl*iso*emetine on methylation, and is therefore *N*-methyl*iso*cephaeline.

Two grams of the pure isomeride, melting at 196—197° (corr.), were dissolved in a solution of 0·5 gram of sodium in 50 c.c. of

fusel oil, boiling at 130—133°, and boiled for two hours under a reflux condenser with 1·25 grams of anhydrous sodium methyl sulphate. On working up the product in the usual way (compare, for instance, T., 1914, **107**, 1623), 1·4 grams of the phenolic base were recovered, and 0·23 gram of *N*-methyl*iso*emetine was obtained. This base melted at 152—153° (corr.) alone or when mixed with the methylation product of *iso*emetine; the specific rotatory power in chloroform solution was found to be $[\alpha]_D -47·6°$ ($c=1·125$).

N-*Methyl*iso*emetine Methiodide.*

Twenty-five grams of *iso*emetine hydrobromide were dissolved in 625 c.c. of hot water, cooled, mixed with 50 c.c. of methyl iodide and 25 grams of anhydrous sodium carbonate, and heated on the water-bath. After one and three-quarter hours, the insoluble matter, which was viscous and amorphous at first, had become crystalline, and was collected. It amounted to 21·3 grams, and formed colourless, well-defined, oblong prisms which melted at 290—292° (corr.) after drying at 100°. This salt is very sparingly soluble in cold water.

Found, in air-dried salt, loss in a vacuum=2·4; in dried salt, I=32·4.

$C_{32}H_{48}O_4N_2I_2,H_2O$ (796·4) requires $H_2O=2·3$ per cent.

$C_{32}O_{48}O_4N_2I_2$ (778·4) requires I=32·6 per cent.

The specific rotatory power of the hydrated salt was determined in aqueous solution:

$$\alpha_D + 0·6°;\ c=0·324;\ l=2\text{-dcm.};\ [\alpha]_D + 92·6°.$$

The mother liquors from the crystalline methiodide were concentrated, and deposited 6·5 grams of pale orange-brown resin, which became quite hard, but was not obtained in a crystalline form. The crystalline and amorphous salts were found to give the methine in approximately equal yield.

N-*Methyl*iso*emetinemethine*, $C_{32}H_{46}O_4N_2$.

29·2 Grams of *iso*emetine hydrobromide were converted into methyl*iso*emetine methiodide by the method described above, and the combined crystalline and amorphous methiodides were converted into the anhydro-base by the method employed for methylemetinemethine (T., 1917, **111**, 445). The crude methine was neutralised with 20 per cent. aqueous oxalic acid, and gave 21·1 grams of neutral oxalate in several crops, that is, 75·4 per cent. of the theoretical yield.

*Methyl*iso*emetinemethine oxalate* crystallises from water in

colourless prisms of an elongated diamond shape which are very easily soluble in water. The air-dried salt contains $4H_2O$ and melts at 122—127° (corr.); after drying at 100°, the salt melts at 133—134° (corr.).

Found, in air-dried salt: $H_2O = 10 \cdot 8$, $10 \cdot 7$.

$C_{32}H_{46}O_4N_2,C_2H_2O_4,4H_2O$ (684·6) requires $H_2O = 10 \cdot 5$ per cent.

Found, in air-dried salt: $C = 66 \cdot 4$, $66 \cdot 4$, $66 \cdot 5$, $66 \cdot 5$; $H = 7 \cdot 9$, $7 \cdot 9$, $7 \cdot 9$, $7 \cdot 9$.

$C_{32}H_{46}O_4N_2,C_2H_2O_4$ (612·6) requires $C = 66 \cdot 6$; $H = 7 \cdot 9$ per cent.

The specific rotatory power of this salt was determined in aqueous solution:

$$\alpha_D + 0 \cdot 35^\circ;\ c = 4 \cdot 153;\ l = 2\text{-dcm.};\ [\alpha]_D + 4 \cdot 2^\circ.$$

*Methyl*iso*emetinemethine methiodide* separates as a crystalline powder when a concentrated ethereal solution of the methine, prepared by regeneration from the pure oxalate, is warmed with methyl iodide. The salt, so prepared, began to sinter at 155° and effervesced at 163° (corr.); when moistened with cold water, it first became gummy and then crystallised; it appeared to contain methyl iodide of crystallisation, for when it was added to boiling water effervescence took place, and an odour of methyl iodide was observed. The hot aqueous solution deposited the salt on cooling in silky needles, which melt at 178° (corr.) after drying at 100°, and effervesce at about 180°.

Found, in air-dried salt: loss at $110^\circ = 4 \cdot 0$.

$C_{34}H_{52}O_4N_2I_2,2H_2O$ (842·4) requires $H_2O = 4 \cdot 3$ per cent.

Found, in dried salt: $I = 31 \cdot 6$.

$C_{34}H_{52}O_4N_2I_2$ (806·4) requires $I = 31 \cdot 5$ per cent.

Oxidation of iso*Emetine. Formation of Methylpsychotrine and Rubremetine.*

(1) *With One Molecular Proportion of Iodine.*—This oxidation was carried out essentially in the same way as that of emetine (T., 1917, **111**, 434), but the isolation of methylpsychotrine as hydrogen oxalate was complicated by the fact that *iso*emetine hydrogen oxalate also crystallises from moist alcohol, whereas emetine hydrogen oxalate does not.

Twenty grams of *iso*emetine hydrobromide were recrystallised from 50 c.c. of water, when 19 grams separated. After removing this, the mother liquor gave further small crops of the same salt on concentration, and eventually a liquor which no longer deposited crystals. This was shaken with aqueous sodium hydroxide and ether, and the regenerated base, amounting to 0·04 gram, was con-

verted into the hydrogen oxalate in alcoholic solution, when 0·02 gram of colourless, somewhat spongy crystals was obtained, which, after drying at 100°, sintered at 145°, and gradually melted up to about 200°. The melting point indicates that this hydrogen oxalate did not consist wholly of methylpsychotrine hydrogen oxalate, whence the original hydrobromide contained less than 1 per cent. of methylpsychotrine.

Nine grams (part of the 19 grams) of purified *iso*emetine hydrobromide were then converted into the base and oxidised with 3·2 grams of iodine in 80 c.c. of absolute alcohol by heating for three and a-half hours at 100°.

The product was mixed with dilute sulphurous acid, evaporated to about half its volume, mixed with aqueous sodium hydroxide, and extracted with chloroform. The chloroform extract was completely extracted with dilute hydrochloric acid, dried, and distilled, when it left 2·3 grams of dark brown resin. This was extracted with small quantities of boiling water, and the filtered extracts were mixed with a small quantity of aqueous potassium iodide, when 0·9 gram of rubremetine hydriodide separated in minute red needles, which, after drying at 100°, began to melt at 177° (corr.) either alone or when mixed with rubremetine hydriodide prepared by the oxidation of emetine. The identification of the salt with rubremetine hydriodide was further confirmed by analysis. (Found, in air-dried salt, $H_2O = 13·5$; in dried salt, $I = 21·3$. Calc.: $H_2O = 13·0$; $I = 21·2$ per cent.)

The hydrochloric acid extract of the chloroform extract was mixed with aqueous sodium hydroxide and extracted with chloroform. The chloroform residue was converted into the hydrobromide, when 5·0 grams of *iso*emetine hydrobromide were recovered. The mother liquors, shaken with aqueous sodium hydroxide and ether, gave 0·7 gram of base, which was dissolved in alcohol containing 0·4 gram of hydrated oxalic acid. On inoculating with methylpsychotrine hydrogen oxalate, 0·13 gram of nearly colourless crystals, melting at 140—145° (corr.), separated. For purification, the base was regenerated from this material and again converted into hydrogen oxalate, when 0·08 gram was obtained, which melted at 145—150° (corr.), methylpsychotrine hydrogen oxalate melting at 150—155° (corr.) in the same bath, and a mixture of the two substances intermediately. The aqueous solution of the salt showed the blue fluorescence characteristic of methylpsychotrine salts. A determination of the specific rotatory power gave a low value, $[\alpha]_D + 33°$ ($c = 1$), and consequently further evidence of the identity of the substance was required. Accordingly, the base was regenerated, neutralised with dilute sulphuric

acid, and the solution evaporated to dryness, then moistened with absolute alcohol and evaporated to dryness several times. Finally, it was dissolved in a few drops of absolute alcohol and inoculated with methylpsychotrine sulphate monohydrate, when a colourless, crystalline powder separated, which melted at 245° (corr.), methylpsychotrine sulphate melting at 248° (corr.), and a mixture of the two substances at 246° in the same bath.

(2) *With Ferric Chloride.*—Two grams of *iso*emetine hydrochloride were oxidised with an aqueous solution of 40 grams of commercial hydrated ferric chloride, the details of manipulation being the same as previously described for the oxidation of emetine with ferric chloride (T., 1914, **105**, 1627). After crystallisation from water, 0·45 gram of crude rubremetine hydrochloride was obtained. This was purified in the manner previously described, and identified by comparison with a specimen prepared from emetine.

Action of Sodium Amyloxide on iso*Emetine.*

The base liberated from 3 grams of *iso*emetine hydrobromide was dissolved in a solution of 1·0 gram of sodium in 50 c.c. of fusel oil (b. p. 130—133°), and boiled for fourteen hours under a reflux condenser. After the addition of 6 c.c. of hydrochloric acid and 20 c.c. of water, the fusel oil was removed by steam distillation, and the non-phenolic and phenolic bases were recovered and separated in the usual way. The latter—amounting to 0·3 gram of yellow resin—were neglected, whilst the non-phenolic bases were found to consist almost entirely of *iso*emetine, for when treated with hydrobromic acid they gave 2·3 grams of pure *iso*emetine hydrobromide, the mother liquors containing only a trace of material.

Emetine, when treated in a similar manner, was also mainly recovered unchanged, except in so far as it had become hydrolysed, and no evidence of the formation of *iso*emetine could be obtained.

*Preparation and Separation of α- and β-*N*-Methylemetine Methiodides.*

Ten grams of emetine hydrobromide were dissolved in 250 c.c. of hot water, and the solution, after cooling to some extent, was mixed with 20 c.c. of methyl iodide and 10 grams of anhydrous sodium carbonate. It was then heated on the water-bath under a reflux condenser so that the methyl iodide boiled. After three hours crystals began to form, and gradually increased in quantity; after boiling for a fourth hour, the excess of methyl iodide was

removed by distillation and the liquor filtered from the first crop of crystals—8·0 grams; m. p. 210—220°; $[\alpha]_D - 6°$. On cooling, the mother liquor deposited a second crop of crystals—2·6 grams; m. p. 220—260°; $[\alpha]_D + 32·4°$—whilst a third fraction was obtained by extraction with chloroform as a nearly colourless resin (0·7 gram) which deposited crystals after solution in water. After recrystallising the first crop from water twice, the previously known α-methiodide was obtained in a pure state; it had the melting point previously recorded, namely, 225—226° (corr.), and formed prisms containing between 3 and $4H_2O$. (Found: $H_2O = 7·9$. Calc. for $3H_2O$, 6·3; for $4H_2O$, 8·5 per cent.) The specific rotatory power was determined in aqueous solution:

$$\alpha_D - 0·23°;\ c = 1·145;\ l = 2\text{-dcm.};\ [\alpha]_D - 10·0°.$$

After prolonged fractional crystallisation, there were obtained 5·35 grams of this salt in a pure state, 2·6 grams less pure, melting at 210—220°, various small crops melting between 220° and 260°, and 0·45 gram of the pure *β-methiodide*.

α-N-Methylemetine methochloride was prepared from the α-methiodide by double decomposition with silver chloride, concentration of the filtered solution to a syrup, and precipitation with acetone, when it formed small, colourless needles which melted at 133° (corr.) after drying at 100°, and at 200° (corr.) after drying at 110°.

Found, in air-dried salt: loss at 100—110° = 15·2.

$C_{32}H_{48}O_4N_2Cl_2,6H_2O$ (703·6) requires $H_2O = 15·3$ per cent.

Found, in salt dried at 100—110°: C = 64·2, 64·2; H = 8·1, 8·0.

$C_{32}H_{48}O_4N_2Cl_2$ (595·5) requires C = 64·5; H = 8·1 per cent.

The specific rotatory power of this salt was determined in aqueous solution:

$$\alpha_D - 0·18;\ c = 3·986;\ l = 2\text{-dcm.};\ [\alpha]_D - 2·3°.$$
$$\alpha_D - 0·18;\ c = 1·993;\ l = 2\text{-dcm.};\ [\alpha]_D - 4·5°.$$

β-N-Methylemetine methiodide forms long, flat plates from water, which melt at 262° (corr.) after drying at 100°. Like the α-salt, it is easily soluble in hot, but very sparingly so in cold water.

Found, in air-dried salt: $H_2O = 5·2$.

$C_{32}H_{48}O_4N_2I_2,2\frac{1}{2}H_2O$ (823·4) requires $H_2O = 5·5$ per cent.

Found, in salt dried in a vacuum: C = 49·6; H = 6·3.

$C_{32}H_{48}O_4N_2I_2$ (778·4) requires C = 49·3; H = 6·2 per cent.

The specific rotatory power was determined in aqueous solution:

$$\alpha_D + 1·15°;\ c = 0·844;\ l = 2\text{-dcm.};\ [\alpha]_D + 68·1°.$$

Formation of N-*Methylemetinemethine from the β-Methiodide.*

0·5 Gram of the β-methiodide was converted into the methine by the method used for the α-methiodide (T., 1917, **111**, 445). The crude tertiary base, extracted by ether (0·27 gram), was dissolved in alcohol and neutralised with oxalic acid, when 0·12 gram of methylemetinemethine oxalate crystallised in prisms. It melted at 82—83° (corr.), a mixture with the salt prepared from the α-methiodide melting at the same temperature.

For further identification, the water of crystallisation was estimated (Found: $H_2O = 18·9$. Calc.: $H_2O = 18·1$ per cent.), and an approximate determination of the specific rotatory power was made [Found: $[\alpha]_D$ $-19·5°$ ($c = 1·2$ in water); previously found for salt from α-methiodide, $[\alpha]_D$ $-24·6$]. It was also observed that the methine from the β-methiodide gave a hydrochloride, which crystallised from absolute alcohol in plates. A similar salt had previously been obtained from the methine prepared from the α-methiodide, by the following method.

N-*Methylemetinemethine Hydrochloride.*

A quantity of the base, regenerated from the pure oxalate to ether, was dissolved in dilute hydrochloric acid and evaporated to dryness. It was next dissolved in absolute alcohol and evaporated to dryness, this operation being repeated several times. It was then dissolved in a small volume of absolute alcohol, when it separated in colourless, quadrilateral plates, which melted at 236° (corr.) after drying at 100°. This salt is very easily soluble in water.

Found, in air-dried salt: loss at 105° = 2·4, 3·7.

$C_{32}H_{46}O_4N_2,2HCl,H_2O$ (613·4) requires $H_2O = 2·9$ per cent.

Found, in salt dried at 105°: Cl = 11·5, 11·5.

$C_{32}H_{46}O_4N_2,2HCl$ (595·5) requires Cl = 11·9 per cent.

In conclusion, my thanks are due to Mr. E. C. S. Jones for assistance in this investigation.

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XXVII.—*The Supposed Formation of Ergotoxine Ethyl Ester from Ergotinine. A Correction.*

By GEORGE BARGER and ARTHUR JAMES EWINS.

SOME years ago (T., 1910, **97**, 284) we obtained a crystalline phosphate by boiling ergotinine in alcoholic solution with phosphoric acid, and we concluded that the salt was the phosphate of ergotoxine ethyl ester. This is not so; it is the phosphate of ergotoxine itself. Ergotoxine, $C_{35}H_{41}O_6N_5$, is the hydrate of ergotoxine, $C_{35}H_{39}O_5N_5$ (Barger and Carr, T., 1907, **91**, 337), and at the time of our previous work the phosphate of ergotoxine (the first salt to be crystallised) had been obtained exclusively in the form of fine needles (T., 1910, **97**, 286, Fig. 2), whilst our supposed ester salt crystallised in broad plates (*loc. cit.*, Fig. 1). Similar differences of crystalline form were observed in the hydrochlorides (*loc. cit.*, Figs. 3 and 4), and oxalates, prepared from the two phosphates. (On the other hand, each pair of salts had approximately the same melting point.) We chiefly relied, however, on an analysis (1 per cent. more carbon than in ergotoxine phosphate, as calculated) and a Zeisel determination of the ethoxy-group. (Found, 5·97. Calc., 5·82 per cent.)

Some years later, Mr. F. H. Carr and Dr. F. L. Pyman determined the methoxy- and methylimino-groups in ergotoxine and in ergotinine, and drew the conclusion that both alkaloids contain one *O*-methyl and one *N*-methyl group. In that case we ought to have found two alkyloxy-groups in the ester, as Messrs. Carr and Pyman pointed out to us. Their determinations were as follows:

Ergotinine.—The substance was of good colour and crystalline appearance, and melted at 231°. It suffered no appreciable loss on drying even at 130°.

1. 0·4051 gave 0·1241 AgI below 180°. OMe = 4·0.
   and 0·1004 AgI above 290°. NMe = 3·1.

2. 0·3019 gave 0·0851 AgI below 180°. OMe = 3·7.
   and 0·0942 AgI above 290°. NMe = 3·9.

3. After a blank distillation of the hydriodic acid yielding 0·0053 AgI:

0·1457 gave 0·0258 AgI below 180°. OMe = 2·3.

4. After a blank distillation of the hydriodic acid yielding 0·0123 AgI:

0·4128 gave 0·0794 AgI below 180°. OMe = 2·5.
and 0·1139 AgI above 290°. NMe = 3·4.

5. After a blank distillation of the hydriodic acid (10 c.c.) yielding 0·0098 AgI and the subsequent addition of 5 c.c. of acetic anhydride:

0·4127 gave 0·1548 AgI below 180°. OMe = 4·9.
and 0·0688 AgI above 290°. NMe = 2·1.

6. After a blank distillation of the hydriodic acid (10 c.c.) yielding 0·0218 AgI, and the subsequent addition of 5 c.c. of acetic anhydride:

0·4130 gave 0·1401 AgI below 180°. OMe = 4·5.
and 0·0764 AgI above 290°. NMe = 2·3.

7. Blank distillation with 10 c.c. of hydriodic acid for one hour gave 0·0027 AgI, after addition of 5 c.c. of acetic anhydride, and a double distillation for two hours gave 0·0183 AgI, after a further double distillation for two and one-third hours gave 0·0025 AgI:

0·4966 gave 0·1501 AgI below 180°. OMe = 4·0.
and 0·0713 AgI above 290°. NMe = 1·7.
$C_{35}H_{39}O_5N_5$ requires OMe = 5·1; NMe = 4·8 per cent.

Ergotoxine Phosphate.—

1.	0·3976	gave	0·1204 AgI	at 140—195°.	OMe = 4·0.
2.	0·3926	,,	0·1614 AgI	,, 140—195°.	OMe = 5·4.
3.	0·2302	,,	0·0732 AgI	,, 140—195°.	OMe = 4·2.
4.	0·3954	gave	0·1055 AgI	below 180°.	OMe = 3·5.
		and	0·0663 AgI	above 290°.	NMe = 2·1.
5.	0·3914	gave	0·0982 AgI	below 180°.	OMe = 3·3.
		and	0·0678 AgI	above 290°.	NMe = 2·0.
6.	0·1420	gave	0·0494 AgI	below 180°.	OMe = 4·6.
		and	0·0364 AgI	above 290°.	NMe = 3·2.

Specimen No. 1 was prepared from ergotinine, the rest from ergot. Nos. 4–6 were dried at 100° and analysed with the addition of acetic anhydride. The melting point was 187—188°.

0·1482, dried at 100° (mixed with CuO), gave 0·3120 CO_2 and 0·0900 H_2O. C = 57·4; H = 6·8.
$C_{35}H_{41}O_6N_5,H_3PO_4$ requires C = 57·9; H = 6·1; OMe = 4·3; NMe = 4·0 per cent.

On receipt of the above data we re-examined the action of alcoholic phosphoric acid on ergotinine, on a larger scale than was originally possible. We were able to transform the salt, first obtained as needles, into plates by recrystallisation from alcohol.

One gram of ergotinine was suspended in 15 c.c. of absolute alcohol, and rather more than one molecular proportion of syrupy phosphoric acid was added. On heating under reflux on the water-

bath the ergotinine dissolved, but after a total heating of thirty to forty-five minutes the solution became almost solid with a mass of prismatic needles, which were collected.

The yield was 0·95 gram, or 80 per cent. of the theoretical; the melting point, 189—190°. After drying at 100°:

0·5720 gave 0·0246 AgI (two hours at 140—150°). OMe=0·56.

On recrystallisation from alcohol, plates were formed, melting at 190°, which were analysed:

0·4216 gave 0·0412 AgI (two hours at 150°). OMe=1·3.

From these experiments we conclude that the phosphate was that of ergotoxine, and that no ethyl ester grouping was present, for it would have been readily removed under the analytical conditions employed.

We next examined the action of hydriodic acid on ergotinine, using in each case 10 c.c. of acid (D 1·7) and 5 c.c. of acetic anhydride, the bath being heated for two hours at the temperature intervals indicated.

A. Ergotinine, older (less pure) specimen:

0·4127 gave 0·1259 AgI at 150—195° and 0·0389 AgI at 340—350°. Total AgI=0·1648. OMe=5·3 *or* NMe=4·9.

B. Ergotinine, purer specimen:

0·4129 gave 0·0105 AgI at 140—145°, 0·1333 AgI at 180—200°, and 0·0303 AgI at 300—370°. Total AgI=0·1741. OMe=5·6 *or* NMe=5·2.

$C_{35}H_{39}O_5N_5$ requires OMe=5·1; NMe=4·8 per cent.

We have calculated our results from the total silver iodide formed, for we believe that only one methyl group is present, and think that this methyl group is attached to nitrogen. Messrs. Carr and Pyman's six analyses, in which heating was continued to 290°, when calculated as NMe only, give the mean 6·4 per cent., which is one-third more than the theoretical. In our opinion the amount of silver iodide is, however, insufficient to account for a methoxy- as well as a methylimino-group. There is abundant evidence that many methylimino-groups give off part of their methyl as methyl iodide on merely boiling with hydriodic acid, particularly if carbonyl groups are adjacent (Busch, *Ber.*, 1902, **35**, 1565; Goldschmiedt and Hönigschmid, *Ber.*, 1903, **36**, 1850; *Monatsh.*, 1906, **27**, 849; Kirpal, *Ber.*, 1908, **41**, 819). Decker (*Ber.*, 1903, **36**, 2895) has pointed out that in this way *N*-alkyl may be mistaken for *O*-alkyl, and Herzig (*Monatsh.*, 1908, **29**, 295) states that with nitrogenous substances, unless the formation of silver iodide begins soon after the hydriodic acid boils, and proceeds rapidly to an end, it is unsafe to conclude that a methoxyl group is present. In

our own experiments the evolution of methyl iodide from the boiling acid was slow and incomplete, whence our conclusion, that ergotinine and ergotoxine contain one *N*-methyl group, but no methoxy-group.

We desire to thank Messrs. Carr and Pyman for having directed our attention to the error in our former paper, and for having placed their analytical results at our disposal.

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XXVIII.—*Interaction of Formaldehyde and Carbamide.*

By AUGUSTUS EDWARD DIXON.

IN a paper by Dixon and Taylor on the interaction of aldehydes and thiocarbamides (T., 1916, **109**, 1244), it is mentioned in passing that a molecular mixture of carbamide and formaldehyde, when condensed by means of hydrochloric acid, yielded a substance, apparently identical with the methylenecarbamide obtained by Hemmelmayr (*Monatsh.*, 1891, **12**, 94), from carbamide and chloromethyl alcohol. Subsequently—but not until most of the present investigation had been completed—it was learned that several chemists have already studied the interaction between carbamide and formaldehyde (see, for example, Hoelzer, *Ber.*, 1884, **17**, 659; Tollens, *ibid.*, 1896, **29**, 275; Goldschmidt, *ibid.*, 2439; *Chem. Zeit.*, 1897, **21**, 460, 586; Einhorn and Hamburger, *Ber.*, 1908, **41**, 24). In one case only is it necessary to comment on the results.

According to Goldschmidt, carbamide yields, with "excess" of formaldehyde, a compound, $C_5H_{10}O_3N_4$ (that is, $2CH_4ON_2 + 3CH_2O - 2H_2O$), which is formed alike in the presence or in the absence of acids *; and as the yield is theoretical, he concludes that carbamide may thus be determined quantitatively. With these statements, the author's experience does not quite tally; for, in an acidified mixture, the precipitate may not be formed quantitatively; it may have a different composition, or it may not be formed at all. Moreover, in a neutral mixture of the components, even after six months' keeping, no sign of condensation was observed (Expt. 1).

From a slightly acidified solution of carbamide (1 mol.), the condensate, with 0·75 mol. of formaldehyde, is methylenecarbamide;

* Presumably, this means in a neutral solution

with 1 mol. of formaldehyde it is slightly contaminated with Goldschmidt's compound. With $1\frac{1}{2}$ mols. of formaldehyde, and thenceforward up to well beyond 2 mols., the latter compound is the sole product. Further increase of the formaldehyde ratio diminishes the yield, which, at 4 mols., is small, the product being a substance, $C_5H_{12}O_4N_4$; whilst, with 11 mols., condensation ceases.

The precipitates obtained by "catalysing" solutions of carbamide containing variable proportions of formaldehyde, although differing, it may be, largely in composition, exhibit a close general resemblance. They occur in minute, white granules, apparently amorphous, each of which, in plane-polarised light, usually displays a black cross, like that of certain starches. Practically insoluble in all the common solvents, and in cold, dilute mineral acids, they are resolved by heating with the latter into formaldehyde and carbamide; infusible, they decompose at a high temperature, considerably variable with the duration of the preliminary heating (somewhere in the neighbourhood of 240—250°, uncorr.).

From these facts it is concluded that the so-called methylenecarbamide cannot properly be represented by the simple formula, $CO{<}{\begin{smallmatrix}NH\\NH\end{smallmatrix}}{>}CH_2$, but is a dimeride, containing, like Goldschmidt's compound, two carbamide residues in the molecule. Its configuration may be represented as $CO{<}{\begin{smallmatrix}NH\cdot CH_2\cdot NH\\NH\cdot CH_2\cdot NH\end{smallmatrix}}{>}CO$ (I), Goldschmidt's compound being the methylol derivative,

$$CO{<}{\begin{matrix}NH\text{———————}CH_2\cdot NH\\N(CH_2\cdot OH)\cdot CH_2\cdot NH\end{matrix}}{>}CO \text{ (II)},$$

whilst the substance, $C_5H_{12}O_4N_4$, mentioned above, is probably similar, that is, $CO{<}{\begin{smallmatrix}NH\text{———}&CH_2&\text{———}NH\\NH\cdot CH_2\cdot OH&&HO\cdot CH_2\cdot NH\end{smallmatrix}}{>}CO$ (III). The formula, $CO(NMe\cdot CO\cdot NH_2)_2$, proposed by Goldschmidt (*loc. pr. cit.*) for his compound does not seem to be in harmony with its decomposition into carbamide and formaldehyde by dilute acids; it is slowly attacked, too, by hot alkalis, with the evolution of ammonia, but no methylamine was detected.

Ready-formed "methylenecarbamide," when kept in contact with formalin, did not combine with it, to yield the compound II above, nor did this, under like conditions, give the possible derivative, $CO{<}{\begin{smallmatrix}N(CH_2\cdot OH)\cdot CH_2\cdot NH\\NH\cdot CH_2\cdot (CH_2\cdot OH)N\end{smallmatrix}}{>}CO$ (IV); the last compound, in fact, has not been isolated, even in circumstances apparently favourable.

From a neutral solution of carbamide (1 mol.) in formalin (1 mol.), methylolcarbamide, together with a little dimethylolcarbamide, is deposited on concentration in a vacuum over sulphuric acid. The former compound, it would seem, is a near precursor of

"methylenecarbamide"; for, such a solution, if kept for one-and-a-half hours, so as to give the components a little time to combine before treatment with acid (they do not quickly unite in quantitative amount), began to condense nearly twice as soon as a mixture, otherwise similar, but freshly prepared. Moreover, when ready-formed methylolcarbamide, in like circumstances of concentration and of temperature, was acidified to the same extent, condensation started in one-fifteenth of the time required by a freshly-made mixture of carbamide and formaldehyde (Expt. 15). Dimethylolcarbamide, on the other hand, is relatively slow to condense—a fact already noted by Einhorn and Hamburger (*loc. cit.*). The reason, no doubt, is that the dimethylol derivative of 'methylenecarbamide' (IV, above) resists formation in the presence of acids; so that, until time enough has passed for the elimination of a certain amount of formaldehyde, condensation is barred. No doubt, too, the complete stoppage of the carbamide–formaldehyde condensation (see above) by a very large excess of formaldehyde is due to the maintenance of the carbamide in the state of its dimethylol derivative; if the uncondensable mixture is added to a concentrated aqueous solution of carbamide, a precipitate separates forthwith (Expt. 9).

Having regard to the above facts, one may reasonably judge that "methylenecarbamide" results from the decomposition of some compound, generated by the action of, say, hydrochloric acid on methylolcarbamide. Of the stages that must occur, the first is probably the change of $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot OH$ into

$$NH_2 \cdot CO \cdot NH \cdot CH_2Cl,$$

a compound, likely to be unstable, owing to the loss (at least, if water is present) of hydrogen chloride. Through the elimination of hydrogen chloride there originates the residue, $\cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot$, whence, by polymerisation, the compound $CO{<}^{NH \cdot CH_2 \cdot NH}_{NH \cdot CH_2 \cdot NH}{>}CO$ ("methylenecarbamide") could occur. An essentially similar change, in fact, has been observed by Chattaway (T., 1909, **95**, 236), chlorocarbamide, by the loss of hydrogen chloride, polymerising thus:

$$CO{<}^{NH_2}_{NHCl} + CO{<}^{NHCl}_{NH_2} \longrightarrow 2HCl + CO{<}^{NH \cdot NH}_{NH \cdot NH}{>}CO.$$

Really, however, the carbamide–formaldehyde process is somewhat more complex than is here indicated, for, as previously mentioned, molecular proportions of carbamide and formaldehyde do not give pure "methylenecarbamide"; moreover, the condensate of a tolerably pure specimen of methylolcarbamide was markedly contaminated with a substance poorer in nitrogen. Further inquiry

showed that, in the acid condensation of methylolcarbamide, a secondary reaction occurs, the compound being decomposed, to some extent, into carbamide and formaldehyde (a change like that of aldehyde-ammonia, except that the acid completely neutralises the ammonia, whereas it has but little power to fix a base so feeble as carbamide).

Now, an aqueous solution of methylolcarbamide gives, with sodium nitroprusside and phenylhydrazine, no reaction for formaldehyde, nor does it show the reaction for carbamide with mercuric nitrate; neither, when once formed, does "methylenecarbamide" unite with formaldehyde. As the last-named is produced immediately—that is, prior to condensation—the inference was that it must attack the nascent methylenecarbamide residues. If so, and if the proportion of formaldehyde is not sufficient to produce the incondensable dimethylol residues alone, one could foresee that methylolcarbamide, when condensed in the presence of a suitable amount of formaldehyde, should furnish Goldschmidt's compound. On experiment with molecular proportions of the two, this forecast was verified (Expt. 13).

As regards the condensation of carbamide with formaldehyde, a like mechanism is imaginable, since, even in the presence of an acid, the organic components might conceivably unite to form methylolcarbamide. With mixtures only slightly acidified, and hence condensing but slowly, this may be the case; on the other hand, with freely acidified mixtures, the condensation of which may happen within a few seconds, the action must run a different course. Experiment, in fact, has shown that condensation can be accomplished in circumstances where the existence of methylolcarbamide is precluded.

Thus, if carbamide (1 mol.) is dissolved in formalin (1 mol.) previously saturated with hydrogen chloride (and so changed into chloromethyl alcohol), no precipitate appears, a clear syrup being formed instead. If hydrogen chloride is passed through a molecular solution of carbamide in formalin until the clot which first separates dissolves again, a clear syrup is formed, as before. Finally, if hydrogen chloride is led over moist, ready-formed "methylenecarbamide" (or if the latter is added to fuming hydrochloric acid), the solid disappears, giving place to a syrup. Each of these syrups, when poured into water, yields instantly a voluminous, white precipitate of the condensation product. On prolonged exposure in a vacuum over lime and over sulphuric acid, a clear, odourless, resinous material is left; deliquescent, evolving with cold sulphuric acid fumes of hydrogen chloride, and decomposed at once by water, the whole of the contained halogen passing

L* 2

into solution as hydrochloric acid, whilst a condensation product is deposited.

These changes, perhaps, may be represented by the equations:

$$(a)\ CO(NH_2)_2 + CH_2Cl{\cdot}OH \longrightarrow H_2O + NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Cl,$$

$$(b)\ CO{<}^{NH}_{NH}{>}CH_2 + HCl \longrightarrow NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Cl,$$

the product, with excess of water, decomposing as earlier suggested (in the latter equation, for simplicity, the halved formula is used for "methylenecarbamide"). The substances, however, were not pure, nor, by reason of their deliquescence and instability, could any method be devised for their purification.

The possibility that water, in removing the elements of hydrogen chloride, might produce methylolcarbamide (which, of course, would react with the liberated acid), was negatived by the observation that the change occurred equally when the material was added to dilute alkali hydroxide or to a solution of ammonia. Had methylolcarbamide thus been formed, the acid simultaneously being neutralised, no immediate condensation would have followed; although not decisive, these results are consistent with the view already suggested, namely, that "methylenecarbamide" originates from a residue, $\cdot NH{\cdot}CO{\cdot}NH{\cdot}CH_2\cdot$, derived from the compound, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Cl$, or from one of its congeners; that is, in the acid process, with which alone the present paper is concerned.

Dimethylolcarbamide may be produced by evaporating a neutral solution of carbamide in a sufficiency of formalin and crystallising the solid residue from alcohol. The fused material soon decomposes into water, formaldehyde and Goldschmidt's compound, $C_5H_{10}O_3N_4$, an aqueous solution, when acidified, behaving in the same way.

From random acidified mixtures of carbamide and formaldehyde, $C_5H_{10}O_3N_4$ is the product likely to preponderate. The result, however, depends on the conditions imposed; and that different workers, handling these ill-defined, amorphous, insoluble, and generally similar materials should have disagreed, more or less, as to the outcome, is not surprising. In the present research, the results to some extent have been disentangled; it is almost certain, however, that the condensation of carbamide with formaldehyde is a reaction more complex than has been indicated above, both as regards the mechanism and the composition of the products of condensation. It need scarcely be added that, in these reactions, hydrochloric acid is no more a catalyst than is the water or the carbamide or the formaldehyde.

Any definite acid that does not itself decompose carbamide may accomplish the foregoing condensations, either with mixtures of

carbamide and formaldehyde or with the methylolcarbamides, but, of the products obtained with nearly a dozen different acids, no quantitative analyses were made. Carbonic acid was the weakest tried; at the ordinary temperature and under the pressure of one atmosphere, a solution of one molecular proportion of carbamide in one of formalin, previously neutralised, remained clear for two or three days, but gave ultimately a dense precipitate. None of the pure condensation products when kept for an hour in contact with water and urease gave a detectable quantity of ammonia.

EXPERIMENTAL.

Unless it is otherwise stated, the "formaldehyde" used in the experiments described below was commercial formalin containing 37·5 grams of formaldehyde in 100 c.c. of the solution.

Expt. 1.—To 6 grams of carbamide in 100 c.c. of water (free from air), 9 c.c. of formalin were added; the mixture, neutralised with dilute sodium hydroxide and sealed up from contact with the external air, remained clear during six months, at the end of which period the experiment was stopped. Portions removed from time to time and acidified with hydrochloric acid or with sulphuric acid became densely turbid within a few seconds.

Expt. 2.—Without the preliminary neutralisation, Expt. 1 was repeated; in four hours, opalescence was visible, and next day a copious precipitate had separated.

Expt. 3.—Expt. 2 was repeated, 2 c.c. of formic acid solution being added to the mixture, which became turbid in less than half an hour. Next day, the precipitate was removed, washed with boiling water, and dried; its weight amounted to 0·91 of that possible for $C_4H_8O_2N_4$. The product consisted of minute, nearly spherical granules showing in plane-polarised light a black cross, and decomposing with effervescence and browning at about 242° (uncorr.) (in another experiment, at 239°). With rapid heating, the temperature of decomposition may rise by at least 10°. (Found: N=38·3; $C_4H_8O_2N_4$ requires N=38·89 per cent.)

When the carbamide–formaldehyde ratio was exactly 1:1, the percentage of nitrogen in the condensation product was 38·4, the same result also being obtained when a solution containing only 2 per cent. of carbamide was condensed; in both cases, hydrochloric acid was the catalyst used.

Expt. 4.—Carbamide (1 mol.) in tepid aqueous solution and formaldehyde (0·7 mol.), when condensed with hydrochloric acid, yielded a product similar to the preceding, but giving N=38·9 per cent.

A quantity kept for twenty-four hours in contact with a large excess of formalin and then analysed contained about 1 per cent. of nitrogen less than before; hence the ready-formed material does not unite with formaldehyde to produce Goldschmidt's compound ($N=32{\cdot}18$ per cent.). The slight diminution in the nitrogen-content is probably due to the presence of a little paraformaldehyde, an insoluble, gelatinous material, which tends to separate from formaldehyde solutions when acidified and exposed to the air. Always, in fact, when the condensing mixtures contain free formaldehyde, a skin of this substance appears on the surface, and has to be removed; but, even so, the nitrogen-content is often a fraction of a per cent. below the calculated value.

Expt. 5.—A solution of carbamide (1 mol.) in its own weight of water, slightly warmed and mixed with formaldehyde (1·5 mols.), was condensed with hydrochloric acid. Time, three seconds; yield, 0·87 of that calculated for $C_5H_{10}O_3N_4$. (Found: $N=31{\cdot}7$; $C_5H_{10}O_3N_4$ requires $N=32{\cdot}18$ per cent.)

Notwithstanding the large diminution in the percentage of nitrogen, the properties and reactions were much the same as those of "methylenecarbamide." The substance was decomposed by boiling, dilute mineral acids into carbamide and formaldehyde; it was insoluble in all the common solvents; the granules showed in plane-polarised light and under a magnification of 600 diameters the black cross exhibited by the compound mentioned.

Expt. 6.—Carbamide (1 mol.), dissolved in formaldehyde (2 mols.) at the ordinary temperature, was condensed with hydrochloric acid. Time, fifteen seconds (five seconds when the mixture was kept for one and a-half hours previously to acidification); yield, about the same as in the last experiment. Properties, similar; decomposing point, 244°, or with rapid heating 254° (uncorr.). (Found: $N=31{\cdot}6$; $C_5H_{10}O_3N_4$ requires $N=32{\cdot}18$ per cent.)

Expt. 7.—Expt. 6 was repeated with formic acid as "catalyst," a little water being added later to prevent dense solidification. Time, about two minutes; yield, 0·75 of the calculated; decomposing point, with moderately slow heating, 240°. (Found: $N=32{\cdot}1$; $C_5H_{10}O_3N_4$ requires $N=32{\cdot}18$ per cent.)

After five days' contact with formalin in excess, found $N=32{\cdot}2$ per cent.; no combination, therefore, had occurred.

Expt. 8.—Carbamide (1 mol.) in formaldehyde (4 mols.) gave with hydrochloric acid a slight turbidity, not increased by dilution with water. Very slowly, the deposit thickened, and after twenty-four hours was removed; its weight was but 0·35 of that (4·5 grams) of the carbamide employed. The decomposing point was

a shade lower than in the preceding cases (about 233° when put into the apparatus at 150° and 243° when put in at 205°); otherwise, the substance had the properties already described. (Found: N = 29·3; $C_5H_{12}O_4N_4$ requires N = 29·17 per cent.)

This material appears to contain 1 mol. of water more than the compound, $C_5H_{10}O_3N_4$, obtained with a smaller amount of formaldehyde. The experiment was repeated, the mixture being allowed to remain for an hour before treatment with the acid; no difference, however, was noticeable in any way, except that, after forty-eight hours, the yield was 0·48 of the weight of carbamide taken, and that some flakes of paraformaldehyde were present. By sifting, these were removed and the nitrogen was estimated; it was almost the same as before, namely, 29·1 per cent. Possibly, the compound has the structure represented by the formula $NH_2 \cdot CO \cdot N(CH_2 \cdot OH) \cdot CH_2 \cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot OH$, or the methylol groups may be attached to the terminal nitrogen atoms.

Expt. 9.—With 11 mols. of formaldehyde to 1 mol. of carbamide, although the temperature rose perceptibly on the addition of the acid (hydrochloric), the mixture remained clear. Dilution with water or treatment with more acid had no effect, but after a few days' exposure in an open vessel, some paraformaldehyde began to separate. When the clear liquid was poured into a concentrated solution of carbamide, a condensation product rapidly appeared, of which no analysis was made.

In all the preceding experiments, the amount of hydrochloric acid used was roughly 1 c.c. of the concentrated acid (D 1·16) per 6 grams of carbamide; with much larger proportions of acid, the results were as stated below.

Expt. 10.—Two grams of carbamide, in each case, were dissolved in fuming hydrochloric acid: (i) 1 c.c.; (ii) 2 c.c.; (iii) 3 c.c.; (iv) 4 c.c.; (v) 6 c.c. Then, to each of the first four solutions were added 2·5 c.c. of formalin, diluted with the same acid to 4 c.c.; to the fifth, 3 c.c. of formalin; the respective temperatures attained were 55°, 55°, 52°, 48°, and 44°. Soon, (i) became opaque and solidified; (ii), on cooling, changed to a silica-like jelly; (iii) developed presently a few small clots, which later redissolved; (iv) and (v) remained permanently clear; all the solutions, when diluted with water, forthwith became thickly turbid. After remaining for ten days in a vacuum over lime and sulphuric acid respectively, (iv) formed a stiff, almost solid syrup, giving up to water HCl = 23·5 per cent. of its weight.

Expt. 11.—Hydrogen chloride was passed through a cooled solution of carbamide in 1 molecular proportion of formaldehyde, and the resultant clear, viscous syrup poured off from the clot of con-

densation product. In a vacuum, as before, the syrup, after several weeks, changed to a resin, which decomposed instantly with water, giving up to the latter, HCl = 25·4 per cent. On exposure to the air, the resin first deliquesced, yielding a clear, mobile liquid; as more moisture was absorbed, this became turbid, and finally solidified, owing to the separation of a condensation product. The experiment was repeated, the gas being passed until all the clot had redissolved; the syrup, treated as before, gave a clear resin having the properties described above, and yielding to water HCl = 24·5 per cent.

Expt. 12.—Dry hydrogen chloride had no visible effect on dry "methylenecarbamide," but when the latter was moistened and the passage of the gas continued, the solid gave place to a colourless syrup, gradually hardening in a vacuum. To water, the solid product gave up HCl = 27·3 per cent., a condensate separating, in which was found N = 37·85 per cent. (the sample of "methylenecarbamide" taken for experiment contained N = 38·0 per cent.). When added to dilute alkali hydroxide or to a solution of ammonia, the chloro-derivative behaved exactly as towards water, hydrogen chloride being eliminated and neutralised by the excess of alkali present, whilst a condensation product was instantly deposited.

Like results were obtained when carbamide was dissolved in formalin, previously saturated with hydrogen chloride (or mixed with excess of fuming hydrochloric acid), and when "methylenecarbamide" was dissolved in cold, fuming hydrochloric acid, the product in all cases being a syrup, behaving as described above. From the foregoing results, it is evident that carbamide, formaldehyde, hydrogen chloride, and water together produce a balanced system, the equilibrium of which depends on the concentrations of the various components.

Solid carbamide hydrochloride, when exposed to the fumes obtained by rapidly distilling paraformaldehyde, did not appear to undergo any change.

Methylolcarbamide.

The somewhat elaborate procedure recommended by Einhorn and Hamburger (*loc. cit.*) for the preparation of this substance is unnecessary; by exposing for a day or two in an exhausted desiccator a solution of carbamide (1 mol.) in formalin (1 mol.), just neutralised by dilute alkali hydroxide, a viscid, crystalline paste was obtained, from which, after a couple of recrystallisations from alcohol, methylolcarbamide was isolated in brilliant, flattened prisms melting at about 110° (corr.). (Found: N = 30·9; $C_2H_6O_2N_2$ requires N = 31·11 per cent.).

The aqueous solution was odourless, and gave with sodium nitroprusside and phenylhydrazine no reaction for formaldehyde, and with neutral mercuric nitrate no reaction for carbamide. On acidification, however, formaldehyde was detected, both prior to condensation and long after the process appeared to be complete.

Dimethylolcarbamide.

A neutralised solution of carbamide (1 mol.) in a little more than 2 mols. of formalin, when treated as above, yielded dimethylolcarbamide; it had essentially the properties described by Einhorn and Hamburger, including the relatively slow condensation by acids. In moderately concentrated solutions, this process requires approximately minutes, where seconds are needed in the case of the monomethylol analogue. Otherwise, its behaviour in an aqueous solution was the same as that of methylolcarbamide.

The fused material soon began to decompose (m. p. about 123°), water and formaldehyde escaping, and a white, amorphous solid being left; this, when heated alongside a pure specimen of the compound, $C_5H_{10}O_3N_4$, melted at the same moment as the latter, and with similar effervescence and browning (255°, uncorr.; both introduced into the bath at 235°). By condensing an aqueous solution with dilute hydrochloric acid, the same product was obtained as by heating; it gave N=32·8 per cent., whereas $C_5H_{10}O_3N_4$ requires N=32·18 per cent. The end result of these changes may thus be represented:

$$2CO(NH\cdot CH_2\cdot OH)_2 \longrightarrow H_2O + CH_2O + C_5H_{10}O_3N_4.$$

Expt. 13.—Approximately pure methylolcarbamide, when condensed by means of dilute hydrochloric acid, yielded a product containing only 35·5 per cent. of nitrogen ("methylenecarbamide" requires N=38·89 per cent.), the deficit presumably being due, as earlier suggested, to the attack of the methylolcarbamide, when in the act of yielding its normal condensation product, by the formaldehyde which is liberated before that act is complete.

The experiment was repeated, 1 molecular proportion of formaldehyde being first added to the solution of methylolcarbamide; in these circumstances, the solid product was found to consist solely of Goldschmidt's compound. (Found, N=32·25. $C_5H_{10}O_3N_4$ requires N=32·18 per cent.)

Expt. 14.—In order to learn whether the last-named compound might result through an interaction between the two methylolcarbamides, somewhat as follows:

$$NH_2\cdot CO\cdot NH\cdot CH_2\cdot OH + CO(NH\cdot CH_2\cdot OH)_2 \longrightarrow 2H_2O + C_5H_{10}O_3N_4,$$

a molecular mixture of the components, in aqueous solution, was acidified, the mixture (which began to condense in forty seconds) being allowed to remain overnight. Here, if the two jointly condensed, the sole product must be the material containing $N = 32.18$ per cent., whereas, if they condensed independently, the first precipitate would be the mixture referred to in Expt. 13 as containing $N = 35.5$ per cent., to which later the condensate of dimethylolcarbamide ($N = 32.18$ per cent.) would add itself; so that, ultimately, the product must give a figure somewhere between the two. The percentage actually found was 33·35, and when the experiment was repeated, but with 0·75 mol. of dimethylolcarbamide, the figure was 34·6; hence, it is concluded that, in a mixture of methylol- and dimethylol-carbamide, acidified with hydrochloric acid, the two substances condense independently.

Although in the acid condensation of the former, the elimination of formaldehyde prevents the production of pure "methylenecarbamide," yet fused methylolcarbamide soon decomposes, water being evolved, but little or no formaldehyde. In this case, the residue is doubtless free from much contamination with Goldschmidt's compound; no analysis, however, was made.

Expt. 15.—Solutions were prepared (*a*) of methylolcarbamide, (*b*) and (*c*) of carbamide and formaldehyde in molecular proportion. All had the same "carbamide-concentration" (1 gram in 6 c.c.); equal volumes of each, at 13°, were acidified with one-twelfth the volume of concentrated hydrochloric acid. Prior to acidification, however, (*b*) was kept at 13° for an hour and a half. The times elapsing before precipitation were, for (*a*) less than three seconds, for (*b*) twenty-eight seconds, for (*c*) forty-five seconds. Ready-made methylolcarbamide, therefore, condensed at least fifteen times as rapidly as a mixture of its components, which had remained for some five or six minutes, whilst a like mixture, kept beforehand for an hour and a-half, condensed in nearly half the time.

Evidently, the union of formaldehyde with carbamide takes place only by degrees; in fact, a solution, kept for twenty-four hours in a vacuum desiccator, still had a strong odour of formaldehyde. In the presence of barium hydroxide, too, at the concentration recommended by Einhorn and Hamburger, the same phenomenon was noticed.

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[*Received, January* 1*st*, 1918.]

XXIX.—*The Sub-bromide and Sub-chloride of Lead.*

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IN a recent paper (T., 1917, **111**, 29), the author has described a method for the preparation of lead sub-iodide by the action of methyl iodide vapour on lead sub-oxide. As indicated in that paper, the method appears of a somewhat general nature, applicable at least to the preparation of other sub-salts of lead. In the present paper, the method has been used to prepare lead sub-bromide and sub-chloride, the only radical alteration being in the replacement of the methyl haloid by the ethyl compound, owing to the more convenient boiling point of the higher homologue.

Lead Sub-bromide.

The apparatus already described in the previous paper (*loc. cit.*) has, with a few minor alterations, proved quite suitable. The lead sub-oxide was prepared from lead oxalate (Found: Pb = 70·17. Calc.: Pb = 70·18 per cent.) precipitated from an acid solution of lead acetate by the addition of oxalic acid, the actual decomposition of the oxalate into the sub-oxide being carried out precisely as described in the former paper. The alterations in the apparatus to be noted were the replacement of phosphoric oxide as a drying agent by anhydrous calcium chloride, and the introduction of a contriction in the glass tubing leading from the oven to the condenser. The former was a matter of necessity, owing to a temporary shortage of the phosphoric oxide, the latter was devised to facilitate the control of the distillation. Shortly after the ethyl bromide* had been introduced into the apparatus, a little distillate collected at the constriction and formed a most convenient gauge for noting the velocity of distillation. This is a very

* *Purification of the Ethyl Bromide.*—The ethyl bromide was prepared from chemically pure potassium bromide, ethyl alcohol, and sulphuric acid. The distillate was treated with dilute sodium carbonate solution, several times with water, then shaken at least four or five times with concentrated sulphuric acid, and finally with water (owing to a tendency to emulsify, it was often found necessary to wash several times with dilute sodium hydroxide solution before the final washing with water). The bromide was dried over calcium chloride, and fractionated from phosphoric oxide, the fraction of constant boiling point alone being used. This method of purification had to be rigidly followed, otherwise samples of ethyl bromide were obtained that contained traces of some reactive impurity in sufficient quantity to cause appreciable errors when a relatively large amount of the bromide was distilled through the sub-oxide.

essential point, for the ethyl bromide appears to react much less vigorously with lead sub-oxide than does methyl iodide. Thus, in the preparation of lead sub-iodide, about fifty minutes' distillation sufficed to convert the sub-oxide into the sub-haloid, whilst in the present case at least 150 minutes' distillation was required to secure complete reaction. The need for a preliminary heating of the vapour before it enters the reaction bulb is even more necessary than in the case of lead sub-iodide. This was again obtained by passing the vapour through a capillary spiral. The extreme slowness of the reaction naturally leads one to search closely for the temperature at which the ethyl bromide just escaped decomposition. By the process of "bracketing," it was found that the distillation can be safely carried through at 261°, but not higher. At temperatures much lower than this, the last traces of sub-oxide react very sluggishly; for example, at 258°; analysis indicated the presence of 74·1 per cent. of lead ($PbBr$ requires $Pb = 72{\cdot}16$ per cent.), although, by the prolonged absence of the evolution of gas, the reaction appeared quite complete. At 262° gas was evolved until the end of the experiment, the product was much lighter than that obtained in experiments carried out at 261°, and analysis gave $Pb = 70{\cdot}2$ per cent. Undoubtedly there had been incipient decomposition of the bromide vapour, with liberation of bromine and subsequent oxidation of the lead sub-bromide to the normal bromide. Indeed, it may be safely asserted that whenever this evolution of gas continues throughout the experiment, one invariably obtains a product contaminated by more or less lead bromide. After the distillation was completed, the receiver containing the distillate was cooled with liquid ammonia, the apparatus partly exhausted, the receiver sealed off, and the exhaustion continued until the pressure had fallen to about 1 mm. It was found to be unnecessary to continue the exhaustion longer as several experiments showed no trace of a volatile product, such as occurred in the preparation of lead subiodide. On the other hand, the amount of non-volatile carbonaceous matter was sufficiently high to necessitate estimation, generally amounting to from 0·3 to 0·5 per cent. of the weight of the lead sub-bromide.

Method of Analysis.—The mixture of lead sub-bromide, carbonaceous matter, and silica was digested with concentrated acetic acid, then extracted with water; after four extractions the residue was treated with a little hot, very dilute nitric acid, as it was found that the carbonaceous matter otherwise tended to coagulate and retain traces of lead bromide. Two washings with the dilute nitric acid sufficed to remove the whole of the dissolved bromide. The

bromine was then weighed as silver bromide; the silica and carbon were weighed in a Gooch crucible, and after ignition in a muffle the weight of carbon was obtained by difference.

The analytical details of the accompanying experiment will make clear the use to which the knowledge of the percentage of carbon was put in arriving at the percentage of lead in the sample.

Typical Experiment.

Two bulbs each containing about 5 grams of lead oxalate intimately mixed with 2 to 3 grams of powdered silica.

Decomposition took place at a maximum temperature of 340° and maximum pressure of 5 cm. Ethyl bromide: about 15 c.c. Temperature of distillation, 261°. *Remarks.*—Five c.c. of distillate had collected in sixty-five minutes. No gas evolution for the last forty minutes. Duration of distillation, one hundred and thirty-five minutes.

Estimation of Lead:—

Weight of bulb and contents	= 8·6648
,, ,, ,,	= 3·7758
,, ,, carbon, silica, bromide	= 4·8890
Corrected for air displacement	= 4·8910
Weight of silica	= 4·4039
,, ,, carbon (calculated from Br analysis)	= 0·0017
,, ,, bromide used	= 0·4854
,, ,, lead sulphate	= 0·5148
Percentage of Pb	= 72·46

Estimation of Bromine:—

Weight of bulb and contents	= 8·6020
,, ,, ,,	= 3·4394
,, ,, carbon, silica, bromide	= 5·1626
Corrected for air displacement	= 5·1644
,, carbon and silica	= 4·4927
,, substance	= 0·6717
,, AgBr found	= 0·4424
Percentage of Br	= 28· 3

Synopsis of Results.

Experiment.	Duration of distillation.	Absence of gas evolution for	Pb. Per cent.	Br. Per cent.
1	135 min.	40 min.	72·5	28·0
2	122 ,,	20 ,,	71·7	28·4
3	140 ,,	25 ,,	71·6	27·5
4	180 ,,	60 ,,	72·5	27·3
5	180 ,,	20 ,,	72·5	28·4
6	175 ,,	20 ,,	71·7	28·2
7	135 ,,	50 ,,	71·8	28·0
8	135 ,,	65 ,,	72·6	28·0
9	155 ,,	90 ,,	71·9	27·9
		Mean	72·09	27·97
		Calc.	72·16	27·84

The slight fluctuations about the mean undoubtedly arise from the extreme difficulty in (*a*) securing complete absence of oxygen, not only in preparing the sub-oxide, but in the introduction of the ethyl bromide and in the distillation, for example, 0·1 c.c. of oxygen let into the apparatus would cause an error of nearly 0·2 per cent. in the estimation of bromine; (*b*) maintaining the temperature of the oven just below that of incipient decomposition during distillation; and (*c*) securing sufficiently slow velocity of distillation to secure thorough heating of the vapour throughout a lengthy experiment.

Properties of Lead Sub-bromide.—The substance oxidises very slowly, more rapidly if the air is moist. After boiling with water in the air and filtering, very little evidence is obtained in the filtrate either of lead or of bromine, whilst if a saturated solution of the sub-bromide is prepared in the absence of air, there is obtained with hydrogen sulphide a darkening in the colour of the solution, but no precipitate separates; under similar conditions lead bromide gives a heavy, black precipitate. A saturated solution prepared in a vacuum gives with silver nitrate only a faint opalescence.

The colour of the sub-bromide appears to be a distinct gray, and although the presence of 0·3 to 0·5 per cent. of carbonaceous matter must necessarily darken the colour, there is little doubt that the grayish appearance is characteristic of the sub-bromide for the following reasons: (*a*) Whenever analysis gives a higher percentage of bromine than 27·9, that is, whenever oxidation has occurred through the temperature being sufficiently high to liberate bromine from the ethyl bromide with consequent oxidation of the sub-bromide to the normal bromide, the colour changes to a much paler one, the substance becoming at times nearly white.

After a rapid distillation carried out at 300° the product was found to be a pale gray, although the percentage of bromine did not exceed 30·6.

Moreover, such a pale coloured product gives, on extraction with hot water, a copious precipitate with a solution of silver nitrate, a reaction which totally fails when the gray product is used.

(*b*) On heating gray lead sub-bromide in a vacuum for two hours at 370°, the colour becomes distinctly paler, and a rapid extraction with hot water reveals the presence of a considerable amount of lead bromide.

The sub-bromide slowly decolorises bromine water, rapidly on warming to about 50°. The sub-bromide, on treatment with acetic acid, nitric acid, etc., immediately decomposes into lead and lead bromide, and after diluting and boiling, complete solution takes place, except for a small quantity of carbonaceous matter.

Determination of Solubility.—As a further proof of the individuality of the compound, the determination of the solubility of the salt in a vacuum by the conductivity method was used. The apparatus already figured (*loc. cit.*) was again used. Small bulbs of thin glass containing silica and about 0·1 gram of lead sub-bromide were prepared by the usual method, and the purity of the samples was controlled by the analysis of the contents of larger bulbs. The actual procedure already described (*loc. cit.*) was closely followed.

The resistance of a saturated solution of carefully prepared lead bromide at 25° was found to be 22 ohms, remaining constant for two hours.

The mean of two closely agreeing experiments with lead sub-bromide gave the following results:

Resistance of the water before breaking the bulb......	=	26000 ohms.
After breaking the bulb......................................	=	1860 „

this remaining unchanged for several hours.

If the ionic mobilities of the bromine and the lead ions (whether Pb^{+} or Pb_2^{++}) are assumed to be the same as in the case of the normal bromide (76·6 and 71·8 respectively), and if complete dissociation takes place, the solubility of the sub-bromide is 0·4 milli-equivalent per litre. This value is about the same as that for the subiodide already recorded (0·35 milli-equivalent per litre), but in both cases it must be emphasised that the values obtained for the solubility are probably a little high, due to unavoidable traces of the normal salt. Such traces are almost certain to be formed through the action of heat on the sub-salt during the sealing of the bulb, whilst the carbonaceous matter, too, may exert an influence on the solubility.

Lead Sub-chloride.

When the lead oxalate has been completely decomposed into sub-oxide about 10 grams of ethyl chloride thoroughly cooled by liquid ammonia were introduced into the distillation flask. By this means any desired quantity could be rapidly introduced from the tubes. The distillation of the chloride could be rapidly regulated by adjusting the temperature of the water-bath, but owing to the low boiling point of the chloride no effort was made to collect the distillate. The reaction between the sub-oxide and the vapour of the ethyl chloride was very slow, and it was soon found that approximately three hours were required for the distillation and a temperature as high as 311° (as recorded by a standardised thermometer). This is shown in the following table.

TABLE I.

Experiment.	Temperature.	Duration.	Cl. Per cent.
1	261°	85 min.	4·2
2	275	135 „	7·4
3	300	165 „	11·1
4	310–11	165 „	14·4
5	312	160 „	15·0
6	315	180 „	17·2
		Theoretical ...	14·6

The highest temperature at which the distillation may be carried out appears to be 311°, and the duration of the experiment in the neighbourhood of three hours. The slowness of reaction suggested that it might be possible to carry through the experiment without having silica present, as was the case with the sub-iodide. In two experiments it was impossible to detect any difference between samples prepared in the presence and in the absence of silica, and in the majority of the experiments tabulated in table II silica was not used as diluent. The only other change in the procedure was that phosphoric oxide was again used as a drying agent, in order to eliminate any traces of ammonia absorbed by the ethyl chloride when it was being introduced into the apparatus.

Method of Analysis.—A slight modification in the method of estimating lead was necessary owing to the high percentage of carbonaceous matter retained in the reaction bulbs. As a rule the estimation of chlorine revealed the presence of about 2 per cent. by weight of carbonaceous matter. The low value at first found by the old method in the estimation of lead under conditions when the estimation of chlorine led one to expect that a pure

sample of sub-chloride had been obtained, suggested that this carbonaceous matter, impregnated as it would be with lead sulphate, might be exercising a reducing action with a consequent slight loss of lead. Thus in one experiment the percentage of chlorine found was exactly correct, whilst the percentage of lead was 84·4 (calc., 85·4). Two bulbs were then prepared, the lead in one being estimated by the method already described; in the other the sub-chloride was extracted five times with hot dilute nitric acid, the filtrate concentrated in a weighed silica crucible, and finally evaporated with excess of sulphuric acid. The results by the old and the new methods were respectively 83·6 and 85·1 per cent., a duplicate experiment giving identical results. The results recorded in table II were obtained by the modified method for estimating lead, the percentage of chlorine being obtained in a manner similar to that described for the bromide, except that no estimation of silica was necessary.

The analytical results are given in table II.

TABLE II.

Experiment.	Duration of distillation.	Pb. Per cent.	Cl. Per cent.
10	190 min.	85·14	14·24
11	205 ,,	85·30	14·85
12	165 ,,	85·53	14·90
13	210 ,,	85·11	14·60
14	210 ,,	85·17	14·04
15	180 ,,	85·94	14·91
	Mean	85·36	14·59
	Theoretical ...	85·39	14·61

Properties of Lead Sub-chloride.—The colour of the sub-chloride is closely similar to the gray colour of the sub-bromide. It must again be emphasised that the gray appearance does not arise from the presence of the carbonaceous matter, for if the sub-chloride is heated in a vacuum above 400°, it becomes nearly white owing to the reaction:

$$2PbCl \longrightarrow PbCl_2 + Pb,$$

the whiteness of the normal chloride more than compensating for the darkness arising from the presence of an equivalent quantity of lead. The sub-chloride is fairly stable in air, but rapidly decolorises bromine water and permanganate solution.

A saturated aqueous solution of lead sub-chloride prepared in a vacuum gives a faint precipitate with silver nitrate as well as with hydrogen sulphide, strongly contrasting in this respect with

the less readily soluble sub-bromide and sub-iodide. The sub-salt is also readily decomposed by acids.

Determination of Solubility.—As a quantitative proof that the gray substance is not an intimate mixture of lead and lead chloride in molecular quantities, a comparison of its solubility with that of the normal chloride has been made by the conductivity method already described.

Resistance of a solution of lead chloride, three times recrystallised, at $25° = 15{\cdot}9$ ohms, a second determination giving the same result.

A small bulb containing 0·1 gram of lead sub-chloride was broken in a vacuum.

Resistance before the bulb was broken	=	21000 ohms.
,, after ,, ,, ,, ,, ...	=	340 ,,

If one assumes the ionic mobilities of the lead and chlorine ions to be the same as for the normal chloride (71·8 and 75·5 respectively) and that complete dissociation takes place (highly probable if the constitution of the salt is represented by the formula $PbCl$, but subject to correction if the formula should prove to be Pb_2Cl_2), the solubility is found to be 2·2 milli-equivalents per litre.

Summary.

1. Lead sub-chloride and lead sub-bromide have been prepared by the action of ethyl chloride or bromide vapour at 311° and 261° respectively on lead sub-oxide.
2. Both compounds are grey, sparingly soluble, fairly stable in air, but readily oxidised by bromine water.
3. The sub-chloride has a solubility of about 2·2 milli-equivalents per litre, the sub-bromide 0·4 milli-equivalent per litre.
4. The sub-salts are readily decomposed by acid into the normal salt and metal.

Further work on the sub-salts of lead, etc., is still in progress. The author desires to record his appreciation of the facilities placed at his disposal by the Walter and Eliza Hall Trust for the prosecution of this research.

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[*Received, February 13th*, 1918.]

XXX.—*The Structure of Crystalline β-Methylfructoside.*

By Ettie Stewart Steele.

Considering the part played by fructose as a constituent of natural disaccharides and polysaccharides, the simple condensation reactions of the sugar are invested with a special importance. The prosecution of these studies is, however, seriously handicapped by the fact that few crystalline compounds are known to result from such condensations, and further complication is introduced by the recent observation that fructose may react in two forms, one of which is constituted according to the ethylene–oxide type of sugar (Irvine and Robertson, T., 1916, **109**, 1305).

Taking these factors into account, it is evident that the examination of the formation of fructosides is beset with difficulties. Thus, the action of acid methyl alcohol on fructose leads to the production of an uncrystallisable syrup, which Fischer (*Ber.*, 1895, **28**, 1145) originally regarded as essentially methylfructoside, and that this product was a mixture of isomeric fructosides was afterwards shown by Purdie and Paul (T., 1907, **91**, 289), who traced the progress of the condensation by polarimetric observations. The complexity of the reaction between fructose and methyl alcohol was further indicated by the fact that, on methylation followed by hydrolysis, the above mixture of fructosides gave rise to two distinct forms of tetramethyl fructose, one of which is crystalline and the other a colourless syrup. The optical relationships of the solid variety of tetramethyl fructose corresponded with those which might reasonably be expected on the assumption that, during the formation of methylfructoside, the parent sugar had reacted partly in the normal butylene–oxide form, and that this structure was preserved in the alkylated ketose. On the other hand, the nature of the syrupy isomeride remained obscure until it was recognised that fructose, in common with other reducing sugars, is capable of reacting in an entirely different form, containing presumably the ethylene–oxide linking. These views have already received expression (Irvine and Robertson, *loc. cit.*), and the explanation has been put forward that the syrupy methylfructoside described by Fischer contains four isomeric compounds, two of which are derived from the normal and two from the abnormal forms of the parent sugar.

The isolation by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216) of a definite crystalline variety of methylfructoside presents an opportunity to test these views and thus to correlate the results of

the different workers in this field. By ascertaining the behaviour of this pure solid fructoside towards potassium permanganate solution, it has now been shown that the compound belongs to the stable type, and thus corresponds with the ordinary α- or β-varieties of methylglucoside, and the magnitude of the specific rotation of the compound is in agreement with this view. With this point settled, it has been possible to prove that the crystalline variety of tetramethyl fructose is likewise a derivative of the butylene-oxide form of fructose. The proof consists in the fact that Hudson's methylfructoside, on complete methylation and hydrolysis, is converted into a crystalline tetramethyl fructose identical with one of the products obtained by Purdie and Paul on subjecting syrupy methylfructoside to the same series of reactions.

It is thus possible to complete the interpretation of the somewhat complex reactions involved in the condensation of fructose with methyl alcohol. The sugar reacts in large measure in the ethylene-oxide form, giving rise to a highly reactive methylfructoside, but, at the same time, normal condensation takes place to a more limited extent. The condensation must thus resemble in many ways that involved in the formation of sucrose, as it has been shown that the fructose constituent of the disaccharide conforms to the ethylene-oxide sugar type (Haworth and Law, T., 1916, **109**, 1314). There is, in fact, an accumulation of evidence pointing to the idea that most fructose derivatives are constituted according to this plan, but, as already stated, a notable exception is provided by Hudson's crystalline methylfructoside and the tetra-acetyl fructose from which it is prepared, as these compounds are undoubtedly representatives of the stable butylene-oxide type.

The complete relationship between the reactions now correlated may be expressed in the scheme on page 259.

The definite compound *A* is thus a constituent of the mixture *B*, and is the source of crystalline tetramethyl fructose of the stable type.

Incidentally, in the course of the work a certain amount of fresh information has been gained as to the action of acetic anhydride and zinc chloride on fructose. Hudson's view that the reaction yields the tetra-acetate as an intermediate step in the formation of the penta-acetate has been supported. The yield of tetra-acetyl fructose is, however, only moderate even under the best conditions, and a considerable quantity of an uncrystallisable syrup is formed which has the composition of a triacetate. This was at first regarded as a mixture of partly acetylated fructoses, but as the composition and specific rotation were not altered by further action with acetic anhydride or by fractional treatment with solvents, it

$$
\begin{tikzcd}
 & & \text{Fructose} \arrow[dl] \arrow[dr] & \\
 & \begin{array}{c}\text{Mixture of}\\ \text{methylfructosides, } B.\end{array} \arrow[d] & & \text{Tetra-acetyl fructose} \arrow[d] \\
 & \begin{array}{c}\text{Mixture of}\\ \text{tetramethyl methylfructosides}\end{array} \arrow[d] & & \begin{array}{c}\text{Tetra-acetyl}\\ \text{methylfructoside}\end{array} \arrow[d] \\
 & \begin{array}{c}\text{Mixture of}\\ \text{tetramethyl fructoses}\end{array} \arrow[dl] \arrow[dr] & & \beta\text{-Methylfructoside, } A. \arrow[d] \\
\begin{array}{c}\text{Ethylene–oxide}\\ \text{type (syrup)}\end{array} & & \begin{array}{c}\text{Butylene–oxide}\\ \text{type (crystalline).}\end{array} & \begin{array}{c}\text{Tetramethyl}\\ \beta\text{-methylfructoside.}\end{array} \arrow[l]
\end{tikzcd}
$$

would appear to be a definite chemical individual. The compound showed the instantaneous reaction towards potassium permanganate solution which is characteristic of the ethylene–oxide type of sugars, and considering the special reactivity of such compounds, the resistance towards complete acetylation is remarkable. This steric hindrance also extends in some measure to alkylation, as, by treatment with silver oxide and methyl iodide, only one methyl group could be introduced into the compound, although two hydroxyl groups are presumably available for substitution.

In sharp contrast with these results, the crystalline tetra-acetyl fructose of the butylene–oxide type displays no resistance to complete substitution, as it can be readily converted into one variety of penta-acetyl fructose and also forms a fully acetylated methyl fructoside. In one respect, however, the compound is abnormal in that, although belonging to the butylene–oxide type and a true reducing sugar, it fails to display mutarotation. This has already been noted by Hudson, and is now confirmed in so far as repeated attempts to isolate the compound in mutarotatory forms invariably failed. In one sense, it is disappointing to find that tetra-acetyl fructose does not belong to the ethylene–oxide type, as the possibility seemed open that the compound might provide a suitable reagent for the synthesis of sucrose. The structural relationships of the compound, as now elucidated, are shown below, and, taken in conjunction with the constitutional study of sucrose contributed

by Haworth and Law (*loc. cit.*), render this expectation somewhat remote.

Fructose

(treated with acetic anhydride and zinc chloride reacts as) :—

↙ ↘

Butylene-oxide fructose → Tetra-acetyl fructose ↙ ↘

Tetra-acetyl methylfructoside (No steric hindrance). | Penta-acetyl fructose

Ethylene-oxide fructose → Triacetyl fructose ↙ ↘

Further acetylation arrested. | Methyl triacetyl fructose → Further methylation arrested.

Experimental.

Preparation and Methylation of β-Methylfructoside.

The fructose employed was specially pure crystalline material prepared for bacteriological use by the hydrolysis of inulin. The sugar was converted into tetra-acetyl fructose in the usual way and thereafter methylated so as to produce tetra-acetyl β-methylfructoside. On removal of the acetyl groups by the agency of barium hydroxide, pure β-methylfructoside was obtained as described by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216).

To a methyl-alcoholic solution of the fructoside (1 mol.) were added silver oxide (5 mols.) and methyl iodide (10 mols.) in the usual way, and the alkylation, which proceeded normally, was completed by six hours' warming on a water-bath. After filtration from silver iodide and extraction of the residue with boiling methyl alcohol, the solution was evaporated under diminished pressure to a syrup and the total product subjected to a second alkylation, in which the same proportion of the methylating agents was used. In this case no extraneous solvent was necessary as the syrup was freely soluble in methyl iodide. On isolation of the product, tetramethyl β-methylfructoside was obtained as a colourless, mobile syrup, showing practically no action on Fehling's solution until after hydrolysis. The compound was identical with that obtained

by Purdie and Paul by condensing crystalline tetramethyl fructose with methyl alcohol by Fischer's method and the specific rotation displayed by the two preparations show little divergence.

Solvent: methyl alcohol; $c=1{\cdot}220$; $[\alpha]_D -120{\cdot}1$.

Hydrolysis of Tetramethyl β-Methylfructoside.

A 3 per cent. solution of the methylated fructoside in 1·5 per cent. aqueous hydrochloric acid was hydrolysed by heating at 90° for thirty minutes. The solution was neutralised by means of barium carbonate, filtered, evaporated to dryness under diminished pressure, and the residue extracted with boiling ether. After drying and removal of the solvent, the syrup obtained in this way solidified completely to a mass of square plates. After two crystallisations from light petroleum the sugar melted at 92—95°, and showed downward mutarotation in the lævo sense, the permanent value being $[\alpha]_D -85{\cdot}6$. The corresponding constants quoted by Purdie and Paul are m. p. 98—99° and $[\alpha]_D -86{\cdot}7$. It is to be observed, however, that this maximum melting point refers to the pure stereoisomeride, and is thus attained only after repeated crystallisation. An average specimen of tetramethyl fructose melts in the neighbourhood of 95°, and the specimen now described showed no alteration in melting point when mixed with material prepared by Purdie and Paul. The composition of the sugar was confirmed by analysis. (Found, OMe=50·65. $C_6H_8O_2(OMe)_4$ requires OMe=52·54 per cent.)

Action of Acetic Anhydride and Zinc Chloride on Fructose.

Fifty grams (1 mol.) of pure crystalline fructose were added gradually to a solution of 4·5 grams of zinc chloride in 250 c.c. (10 mols.) of acetic anhydride and the mixture was stirred at 0° until the fructose had dissolved. The acetylated sugar was extracted with chloroform as described by Hudson, whereby 45 grams of crystalline material were obtained. Recrystallisation from 98 per cent. alcohol yielded 31·8 grams of pure tetra-acetyl fructose. This compound melted at 129—130°, showed $[\alpha]_D$ in chloroform $-92{\cdot}30$, and did not affect potassium permanganate solution even on prolonged action. Attempts to detect mutarotation in chloroform or aqueous solutions of the compound gave negative results even when chloroform or water were substituted for alcohol as the recrystallising media. The tetra-acetyl fructose obtained in this way showed a constant specific rotation in all appropriate solvents.

Examination of Triacetyl Fructose.—After removal of all crystal-

lisable tetra-acetyl fructose from the product of the preparation just described, a large proportion (47 grams) of syrup remained. In order to remove acetic anhydride, this material was boiled for twelve hours under reflux with a large excess of pure dry methyl alcohol. The solution was then neutralised with barium carbonate, and, after filtration, concentrated in a vacuum. Extraction with chloroform gave a pale yellow syrup, having $[\alpha]_D$ in chloroform $-20{\cdot}42$. Analysis of the syrup, dried in a vacuum, gave an acetyl content of 40·41 per cent., which agrees approximately with the calculated value for a fructose triacetate (42·15 per cent.). Attempts to effect further acetylation of the triacetate by repeating the action of acetic anhydride and zinc chloride in the cold failed entirely. The same proportion of the acetylating reagent was used as in the preparation of tetra-acetyl fructose, and the mixture was stirred at 0° until a homogeneous system was obtained. Examination of the product showed it to be unaltered in composition or specific rotation. Further evidence that the syrup was a homogeneous compound was afforded by the fact that fractional extraction with solvents failed to separate the material into components showing any differences in rotatory power.

The exact constitution of the compound has not been determined, and it is even impossible to characterise it with certainty as a genuine derivative of fructose. The removal of the acetyl groups required prolonged agitation in the cold with $N/10$-barium hydroxide, the unsubstituted sugar thus obtained being a lævorotatory syrup. This, although readily convertible into phenylglucosazone melting at 203—204°, could not be identified as fructose, and, considering the conditions required for the hydrolysis of the triacetate, was doubtless an equilibrium mixture of glucose, fructose, and mannose.

Methylation of Triacetyl Fructose.

The syrup dissolved readily in methyl iodide and was methylated in the usual manner with the following proportions of the reagents: triacetyl fructose (1 mol.), silver oxide (5 mols.), and methyl iodide (10 mols.). After a second alkylation the product, isolated in the usual manner, was a colourless syrup, which reduced Fehling's solution and was therefore not a derivative of methylfructoside. As the most trustworthy indication of composition is given by the methoxyl and acetyl contents, these values were determined. Found, OMe=10·6; OAc=42·86.

$C_6H_8O_2(OMe)(OAc)_3$ requires OMe=9·7; OAc=42·15 per cent.

Solvent.	*c.*	Specific rotation.
Chloroform	2·504	−21·96
Ethyl alcohol	2·230	−21·07

The methylated derivative has thus the composition of a monomethyl triacetyl fructose.

The author desires to express her indebtedness to the Carnegie Trust for a research scholarship, during the tenure of which the above research was conducted, and also to Dr. C. S. Hudson, of the U.S. Department of Agriculture, for specimens of various fructose derivatives which facilitated the work.

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[*Received, March 15th*, 1918.]

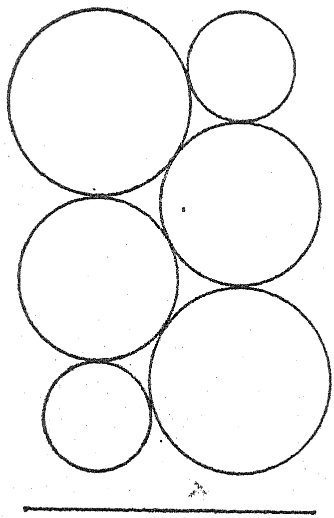
XXXI.—*Contributions to the Theory of Solutions. Solubility Studies in Ternary Mixtures of Liquids.*

By JOHN HOLMES.

AN explanation of the property of relative solubility in binary mixtures of liquids has been put forward in previous papers, based on the ascertained difference in magnitude of the molecular volumes of the constituents of the mixture. It was deduced mathematically that so long as the ratio of the radii of the respective molecules—assuming them to be capable of representation by a spherical surface—did not exceed the proportion 1·618 : 1, the liquids would be miscible in all proportions, and, when the ratio became greater than this value, the mixture would separate into two layers, in each of which the selective distribution of molecules depends on the further increase of this factor until it reaches 2·414 : 1, when the liquids are now completely immiscible. In practice, the relative solubilities of commonly known liquids were found to be in close agreement with these theoretical deductions, and it seemed reasonable to expect that the extension and application of the same principle to three-component systems would afford an explanation of the somewhat similar solubility phenomena therein observed.

Provided that no chemical interaction occurs between the constituents of a ternary mixture of liquids and that no individual liquid influences by its simple physical presence the other constituents, any three liquids the molecular spheres of which have equal radii should be miscible in all proportions. When the spheres are of different sizes, as the ratios of the several radii

increase, the dimensions of the interspaces decrease in magnitude until, as in the case of binary mixtures, a point is reached at which close packing is a maximum. In an equimolecular mixture, which lends itself more readily to mathematical demonstration, this occurs when the radii are as 1·682:1·466:1 (see Figure). It is suggested that when these conditions are fulfilled, the liquids are on the border line between complete and partial miscibility, and that, so long as the ratios between the several radii are not greater than these values, the liquids will be mutually miscible in all proportions. When, however, the respective ratios are greater in magnitude, a complex is formed which will not allow of the same close-packing, but results in the formation of layers of liquid the relative proportions of which depend on the difference in these ratios.



Relative radii, 1 : 1·466 : 1·682.

A further consequence of this method of reasoning follows from the known ratio of radii required for the critical point of solution in binary mixtures. So long as the value of the radial ratio of the two smaller molecules is not greater than 1·618, and the corresponding radius of the larger molecule is greater than 1·682 and does not exceed $(1{\cdot}618)^2$, the mixture should separate into two layers only, but if, on the other hand, the respective ratios are greater than these values, and the greater ratio exceeds the less by more than 1·618 times its value, then the liquids should fall out into three distinct and stable layers.

The object of this communication is to present the results of a preliminary examination into the behaviour of ternary mixtures of liquids from the point of view of these theoretical considerations and of the hypothesis on which this simple law of mixtures is based.

Experimental.

In order to determine the critical point of solution in three-component systems, binary mixtures of liquids were first prepared in equimolecular proportions, and the third liquid then added in

quantity sufficient to produce a permanent cloudiness after vigorous shaking. The point of complete miscibility is capable of determination with a high degree of accuracy, since an excess of one drop in a total volume of 25 c.c. invariably causes separation into layers. The several mixtures were made in calibrated stoppered burettes suspended in a water-bath, the temperature of which was kept constant at 15°. Most of the liquids experimented with had been obtained from Kahlbaum, and the usual methods were resorted to for determining their purity.

Mixtures of the lower primary alcohols with water were prepared in equimolecular proportions referred to the gaseous state. The densities of these mixtures at 15·5°/15·5° were found to be CH_4O aq. (1/1) 0·8898, C_2H_6O aq. (1/1) 0·8676, and C_3H_8O aq. (1/1) 0·8601. The radii of the molecular spheres of methyl alcohol, ethyl alcohol, and *n*-propyl alcohol—represented by the cube roots of the quotients of molecular weight by density—are 1·3, 1·5, and 1·6 respectively when compared with that of water at 15°.

As was to be expected, formic acid, acetic acid, acetone, pyridine, and liquids generally which are miscible in all proportions with water, are similarly miscible with each of the above aqueous-alcoholic mixtures. This applies also to *iso*butyl alcohol, ethyl acetate, aniline, ethyl ether, and the amyl alcohols, the several radii of which are in slight excess of the theoretical value (1·68).

The following are some of the more important quantitative results obtained.

Mixtures with Aniline.

Proportion by volume of the constituents of the mixture.
10 c.c. CH_4O aq. (1/1), 16·1 c.c. C_6H_7N, 3·2 c.c. H_2O
10 c.c. C_2H_6O aq. (1/1), 12·3 c.c. C_6H_7N, 5·2 c.c. H_2O
10 c.c. C_3H_8O aq. (1/1), 10·0 c.c. C_6H_7N, 5·7 c.c. H_2O

Critical molecular mixture.
$C_6H_7N : CH_4O : 2{\cdot}0\ H_2O$
$C_6H_7N : C_2H_6O : 3{\cdot}1\ H_2O$
$C_6H_7N : C_3H_8O : 3{\cdot}9\ H_2O$

The effect of the addition of small quantities of water to these critical mixtures, on the relative proportions of the layers of liquid formed, is very marked. For instance, 20 c.c. of the critical mixture with CH_4O aq. (1/1), to which were added 1·8 c.c. of water, gave after vigorous shaking an upper layer of 6·5 c.c., and a lower layer, coloured with aniline, of 15·3 c.c. Similarly, 20 c.c. of the critical mixture with C_2H_6O aq. (1/1), together with an excess of

1·0 c.c. of water, gave an upper layer of 4·4 c.c., and with 1·9 c.c. of water an upper layer of 7·1 c.c., both lower layers being coloured with aniline. The addition of 2·0 c.c. of water to 20 c.c. of the critical mixture with C_3H_8O aq. (1/1) resulted in an upper layer of 15·5 c.c., which retained the aniline colour, whilst the lower layer was practically colourless; this is the reverse of what happens in the corresponding CH_4O aq. (1/1) mixture. Results very similar to these in character were obtained in other ternary mixtures.

Mixtures with n-*Amyl Alcohol.*

Proportion by volume of the constituents of the mixture.
10 c.c. CH_4O aq. (1/1), 19·25 c.c. $C_5H_{12}O$, 3·55 c.c. H_2O.
10 c.c. C_2H_6O aq. (1/1), 14·65 c.c. $C_5H_{12}O$, 3·95 c.c. H_2O.
10 c.c. C_3H_8O aq. (1/1), 12·0 c.c. $C_5H_{12}O$, 3·7 c.c. H_2O.

Critical molecular mixture.
$C_5H_{12}O : CH_4O : 2{\cdot}1H_2O$.
$C_5H_{12}O : C_2H_6O : 2{\cdot}6H_2O$.
$C_5H_{12}O : C_3H_8O : 2{\cdot}9H_2O$.

The critical molecular mixture of the system ethyl ether with C_2H_6O aq. (1/1) was found to be $C_4H_{10}O : C_2H_6O : 2{\cdot}6H_2O$, a concentration practically the same as that obtained in the corresponding *n*-amyl alcohol mixture.

Mixtures of the foregoing liquids in equimolecular proportions afford no evidence therefore of separation into layers at 15°.

The complexities of ethyl ether and *n*-amyl alcohol, as well as those of the other liquids experimented with above, have been found to be similar to that of water (T., 1913, **103**, 2147); or, if $(H_2O)_n$ be taken as representing the molecule of water in the liquid state, the value of n is the same when applied to the usual formulæ of the other liquids—$(C_5H_{12}O)_n$, $(C_6H_7N)_n$, $(CH_4O)_n$, etc. As will be noticed in the table of liquid complexities given in the communication mentioned above, ethyl ether and *n*-amyl alcohol have molecular volumes greater in magnitude than those of the other liquids in question, and correspondingly greater radii (1·8 approx.) as compared with that of water. This value is somewhat greater than the theoretical (1·68) required for complete solution. This behaviour is analogous, however, to that observed in binary mixtures of liquids in which the critical point of solution varies within somewhat similar limits, according to the nature of the constituents of the mixture and the magnitude of the volume change which occurs on mixing. That such deviation from theoretical requirements should be obtained was therefore to be expected, since most of these mixtures afford volume changes which vary in degree in different mixtures, and must inevitably result in

some disturbance in the initial relationship of the several molecular spheres.

The admixture of the same aqueous-alcoholic mixtures with liquids having molecular radii greater than 1·8, such as methyl iodide, chloroform, benzene, xylene, carbon disulphide, etc., was found to result in the formation of two layers of liquid. The quantitative data obtained in some of these mixtures are as follows:

Mixtures with Methyl Iodide.

Proportion by volume of the constituents of the mixture.	Critical molecular mixture.
20 c.c. CH_4O aq. (1/1) : 1·55 c.c. CH_3I,	H_2O : CH_4O : 0·03 $(CH_3I)_2$.
20 c.c. C_2H_6O aq. (1/1) : 6·8 c.c. CH_3I,	H_2O : C_2H_6O : 0·20 $(CH_3I)_2$.
20 c.c. C_3H_8O aq. (1/1) : 15·3 c.c. CH_3I,	H_2O : C_3H_8O : 0·56 $(CH_3I)_2$.

Mixtures with Benzene.

20 c.c. CH_4O aq. (1/1) : 1·25 c.c. C_6H_6,	H_2O : CH_4O : 0·02 $(C_6H_6)_2$.
20 c.c. C_2H_6O aq. (1/1) : 7·6 c.c. C_6H_6,	H_2O : C_2H_6O : 0·16 $(C_6H_6)_2$.
20 c.c. C_3H_8O aq. (1/1) : 15·6 c.c. C_6H_6,	H_2O : C_3H_8O : 0·40 $(C_6H_6)_2$.

Mixtures with Carbon Disulphide.

20 c.c. C_2H_6O aq. (1/1) : 2·0 c.c. CS_2,	H_2O : C_2H_6O : 0·03 $(CS_2)_4$.
20 c.c. C_3H_8O aq. (1/1) : 7·9 c.c. CS_2,	H_2O : C_3H_8O : 0·15 $(CS_2)_4$.

According to the method adopted in previous communications for determining liquid complexities, methyl iodide and benzene are doubly complexed as compared with water, and have molecular volumes at 15° of 6·90 and 9·84, with corresponding radial ratios of 1·90 and 2·14 respectively. In the same way, carbon disulphide was found to have four times the complexity of water with a molecular volume of 13·31, and a radial ratio of 2·37. The values given above for critical molecular mixtures are referred therefore to the liquid state. The relative proportions of these liquid molecules in the critical mixtures decrease in the same alcoholic mixture as their molecular volumes increase, whilst the solubility of each liquid increases with the molecular volume of the aliphatic alcohol present.

The critical mixtures of the same liquids with water and *iso*butyl alcohol (mol. vol. 5·1 and radial ratio 1·7) are as follows:

Proportion by volume of the constituents of the mixture.
20 c.c. CS_2 : 7·65 c.c. $C_4H_{10}O$: 0·4 c.c. H_2O.
20 c.c. C_6H_6 : 10·35 c.c. $C_4H_{10}O$: 0·6 c.c. H_2O.
20 c.c. CH_3I : 14·8 c.c. $C_4H_{10}O$: 1·1 c.c. H_2O

Critical molecular mixture.
$(CS_2)_4$: $C_4H_{10}O$: 0·26 H_2O.
$(C_6H_6)_2$: $C_4H_{10}O$: 0·29 H_2O.
$(CH_3I)_2$: $C_4H_{10}O$: 0·38 H_2O.

When the liquids in any of these mixtures are present in equimolecular proportions, two layers only are formed, and their behaviour as regards solubility is in general agreement with theoretical requirements.

Of the critical mixtures containing less than equimolecular proportions, those with methyl iodide approximate most closely to the theoretical, just as those containing *n*-amyl alcohol were found to give a corresponding approximation when more than equimolecular proportions are present. The molecular radii of these two liquids, compared with water at 15°, are 1·90 and 1·82 respectively. Hence the radius of the greater molecule in an equimolecular ternary mixture, which is on the border-line between complete and partial miscibility, and of which water and a lower aliphatic alcohol are the other constituents, exceeds that of the smaller molecule by a value intermediate between 1·90 and 1·82, as compared with 1·68 required by theory.

Ternary Mixtures giving Three Liquid Layers.

Little information is to be found in the wide literature relating to the subject of solubility and solutions generally regarding the formation of three stable liquid layers. In commercial analysis, such mixtures are sometimes observed, as, for instance, when castor oil, petroleum, and water or dilute alcohol are shaken together, the castor oil forming an intermediate layer between the aqueous and petroleum layers, in contradistinction to the behaviour of olive oil, which dissolves in the petroleum, so that two layers of liquid only are obtained. Marsh noticed that three layers were formed in the four-component system ethyl ether–water–potassium iodide–mercuric chloride (T., 1910, **97**, 2297), and the equilibrium existing in these mixtures has more recently been investigated by Dunningham (T., 1914, **105**, 368). It is evident that such behaviour of liquids must be classed among the simple facts of solution, and will require adequate explanation by any satisfactory theory of solution. The apparent scarcity of examples of these phenomena is due probably to the fact that no explanation of them is forthcoming from the commonly accepted theories, and that there is little inducement therefore for further investigation in this direction.

According to the principles given above for a simple law of mixtures, the conditions requisite for the formation of three layers in ternary mixtures of liquids must be sought from a consideration of the relative molecular volumes of the liquids present. If the close-packing of molecular spheres in a binary mixture, in which

the ratio of radii is greater than 1·618, results in separation into two layers, it follows that the addition of a third liquid the molecular radius of which is again proportionately greater in magnitude by $(1{\cdot}618)^2$ should result in the formation of three distinct and stable layers. Stated generally, the required ratios for three-layer formation are $(1{\cdot}618+x+y)^2:(1{\cdot}618+x):1$, where x and y are positive.

The difficulty immediately arises as to where a liquid is to be found with a radius greater than that of water by at least $(1{\cdot}618)^2$ or 2·62, since this is the lowest value possible for a three-layer system of which water is one of the constituents. No liquid with so great a molecular volume is given in the table of liquid complexities referred to above. It has been found, however, that members of homologous series, which have hitherto been examined, are similarly aggregated, as, for instance, the aliphatic alcohols and acids and the alkyl iodides, and it is reasonable to assume that members of other series are similar in this respect. From a consideration of the data at present at our disposal, it should be possible to obtain a liquid of suitable molecular volume in the series of paraffin hydrocarbons. There are good grounds for believing that these liquids are doubly aggregated as compared with water (*loc. cit.*), and that their molecular radii increase from *n*-hexane (2·4), *n*-heptane (2·5), etc., as the series is ascended. In these days, the procuring of one of these higher homologues in quantity and sufficiently pure for our purpose is practically impossible. As a compromise, a sample of American petroleum was purified from unsaturated and aromatic compounds and fractionated repeatedly, so as to remove the fractions of lower boiling point. The fraction boiling between 200° and 230° was eventually taken for these experiments. The boiling points of the homologues $C_{11}H_{24}$, $C_{12}H_{26}$, and $C_{13}H_{28}$ are given as 195°, 215°, and 235°, and their calculated radii (assuming double aggregation) are 2·85, 2·92, and 2·99 respectively when compared with water at 15°. It was hoped that the fraction employed would be free from paraffins boiling below 150° (C_9H_{20}, radius 2·7), and the presence of homologues of boiling point higher than 230° is rather advantageous than otherwise to our immediate purpose. In these circumstances, the hydrocarbons present have radii much greater than that required for insolubility in water (2·414), and their relative solubilities, even in methyl alcohol and in ethyl alcohol, are so small that three well-defined and stable layers are readily obtained in the quaternary systems, potassium carbonate–water–methyl alcohol or ethyl alcohol–petroleum.

Among the liquids that have been found to be near the border-

line of complete miscibility with water are aniline, phenol, and nicotine, of which the ascertained radii are approximately 1·7, 1·7, and 1·65 respectively, and each of which is miscible in all proportions within certain limits of temperature. Mixtures of these liquids with the sample of petroleum were made in the proportions of 90, 50, and 10 per cent. by volume, and exactly one-half of the volume of water was added to each. The several liquids were measured into narrow glass tubes which could be hermetically sealed, the total volume of the mixture being from 9 to 10 c.c. in each case. By suspending these tubes in water, the behaviour of the mixtures could be observed up to a temperature of 100°.

Petroleum–Aniline–Water Mixtures.

1. Initial proportions by volume of constituents at 15°

Petroleum	......	33·3
Water	....	33·3
Aniline	....	33·3

On vigorously shaking this mixture at 5°, three layers of liquid are obtained, the middle aqueous layer being of slightly less volume than the upper and lower layers. Between 95° and 100°, the aniline displaces the aqueous layer and rises to the middle position, which it retains after further mixing, the three layers being still practically equal in volume. Gradual cooling causes all three layers to become cloudy, proving that mutual miscibility occurs to some extent. At low temperatures, the aniline falls again to the bottom, and the original condition of equilibrium is resumed.

2. Initial proportions by volume of constituents at 15°

Petroleum	......	6·7
Water	....	33·3
Aniline	....	60·0

The proportions of the three layers obtained after vigorous mixing at 5° are practically the same as the initial volumes. Between 95° and 100°, the aniline layer again displaces the hitherto middle aqueous layer, and on mixing at this temperature, dissolves entirely in the petroleum, thus forming two final layers of liquid. On cooling gradually, the upper petroleum–aniline layer becomes cloudy at 76°, and separates rapidly into two layers, the aniline approaching in volume to its initial proportion and taking up the middle position between the petroleum and aqueous layers. On further cooling, the aniline eventually falls to the bottom into its original position.

3. Initial proportions by volume of constituents at 15°

Petroleum	......	60·0
Water	....	33·3
Aniline	....	6·7

At 5°, the respective layers have the relative proportions

Petroleum layer	62
Water layer	33 .
Aniline layer	5

At 95°, the aniline rises to the middle position and dissolves in the petroleum, forming two layers of liquid. On cooling, the upper layer becomes cloudy again at 55°, and the subsequent behaviour of the mixture on further cooling is similar to that of the preceding mixtures.

Petroleum–Phenol–Water Mixtures.

1. Initial proportions by volume of constituents at 45°

Petroleum	33·3
Water	33·3
Phenol	33·3

On vigorously shaking this mixture at 5°, three layers of liquid are obtained having the approximate proportions

Petroleum layer	35
Water layer.................	22
Phenol layer	43

At 90°, the water and phenol are mutually miscible and form with the petroleum a two-layer system. On cooling, the lower aqueous layer becomes cloudy at 71°, and, at immediately lower temperatures, concentrated phenol separates and falls to the bottom, forming three layers again.

2. Initial proportions by volume of constituents at 45°

Petroleum	6·7
Water	33·3
Phenol	60·0

After mixing at 5°, the relative proportions of the three layers are approximately

Petroleum layer	7
Water layer	13.
Phenol layer	80

Vigorous shaking at 90° results in the formation of two layers of liquid. On cooling, the lower aqueous-phenol layer becomes cloudy at 49°, when concentrated phenol commences to fall to the bottom, and three layers are again obtained.

3. Initial proportions by volume of constituents at 45°

Petroleum	60·0
Water	33·3
Phenol	6·7

At 5°, the relative proportions of the three layers obtained after mixing are

Petroleum layer	62
Water layer	31.
Phenol layer	7

Above 63°, two layers only are

formed, but below this temperature phenol separates, and three stable layers are again obtained.

Petroleum–Nicotine–Water Mixtures.

1. Initial proportions by volume of constituents at 15°

Petroleum	......	33·3
Water	....	33·3
Nicotine	....	33·3

After vigorous shaking at 5°, this mixture of liquids separates into two layers having the relative proportions

Petroleum layer	36
Aqueous-nicotine layer ...	64

When the mixture is heated to 62°, the lower aqueous layer becomes cloudy and separates rapidly into two layers, a lower layer coloured with nicotine and an intermediate and practically colourless aqueous layer which increases in volume as the temperature rises until, at 90°, the relative proportions are

Petroleum layer	41
Water layer	26
Nicotine layer	33

On mixing at the latter temperature, two layers are again formed, due to the nicotine dissolving in the petroleum. The observed proportions of the layers were now

Petroleum–nicotine layer	67
Aqueous layer	33

Both layers remain clear at temperatures above 63°, but at immediately lower temperatures the nicotine begins to separate from the petroleum and falls to the bottom of the tube, leaving at first a colourless intermediate aqueous layer, which, however, on further cooling, mixes with the nicotine, and the liquids resume their original equilibrium of two layers.

2. Initial proportions by volume of constituents at 15°

Petroleum	......	6·7
Water	....	33·3
Nicotine	....	60·0

At 5°, this mixture of liquids forms two layers in the relative proportions

Petroleum layer	8
Aqueous-nicotine layer	92

On raising the temperature to 67°, a cloudiness appears in the aqueous layer, and three layers are formed which at 90° have the relative proportions

Petroleum layer	8
Aqueous layer	9
Nicotine layer	83

. At 100°, the lower nicotine layer rises to

the middle position and dissolves in the petroleum, so that on mixing at this temperature two layers again are formed in the proportions

Petroleum–nicotine layer...	75
Aqueous layer	25

On cooling, the nicotine commences to separate from the petroleum and fall to the bottom of the tube at 68°, and its general behaviour at lower temperatures is similar to that in the preceding mixture. Very gradual cooling of this mixture results in the formation of four layers at some temperatures. These consist of a small and colourless petroleum layer, then a large layer of petroleum and nicotine, and below these in order a colourless, aqueous layer and at the bottom a concentrated nicotine layer. These layers, however, were clearly metastable, and on mixing gave two stable layers only.

3. Initial proportions by volume of constituents at 15°	Petroleum	60·0
	Water	33·3
	Nicotine	6·7

At 5°, the proportions of the two layers formed were

Petroleum layer	60
Aqueous-nicotine layer ...	40

Somewhat similar results were obtained with this mixture; the lower aqueous layer becomes cloudy at 76°, and follows the same procedure as in the preceding mixtures.

It will be noticed that at some concentrations the foregoing mixtures of liquids form two layers only, which, within a limited range of temperature, yield three-layer systems, proving how close is the relationship of the molecular volumes of the several liquids to that required by theory for partial miscibility.

These results prove that our theoretical deductions have some foundation in fact, and that with further knowledge of molecular weights in the liquid state it may be possible to predict a three-layer system in ternary mixtures as readily as a two-layer system in the case of binary mixtures of liquids.

The following results were obtained in the three-component system petroleum–nitrobenzene–water:

1. Initial proportions by volume of constituents at 15°	Petroleum	33·3
	Water	33·3
	Nitrobenzene ...	33·3

On vigorously shaking these liquids at 5°, three layers separate in the approximate proportions

Petroleum layer	25
Water layer	32
Nitrobenzene layer	43

. Both top and bottom layers are tinged yellow, proving that petroleum and nitrobenzene are mutually miscible to some extent. On heating to 90° and again mixing, the nitrobenzene dissolves in the petroleum and two layers are formed, the lower of which is practically colourless. On cooling, the nitrobenzene commences to separate from the petroleum at 18°, and at first takes up the middle position, but finally falls to the bottom at about 15°, when the mixture assumes its original condition of equilibrium.

2. When these liquids are mixed in the relative proportions

Petroleum	6·7
Water	33·3
Nitrobenzene	60·0

and

Petroleum	60·0
Water	33·3
Nitrobenzene	6·7

and are vigorously shaken, two layers only are formed, and in each case the upper layer, consisting of petroleum and nitrobenzene, has twice the volume of the lower aqueous layer. No apparent change occurs on heating to 100°.

We have no knowledge at present regarding the molecular volume of nitrobenzene in the liquid state, but, according to the law of mixtures now put forward, the results obtained above are consistent with the view that it is similarly aggregated to aniline and the primary alcohols. Its molecular volume as compared with that of water at 15° is therefore slightly less than that of *n*-amyl alcohol, namely, 5·65, with a radius of 1·78. These values agree fairly well with its relative solubility, for whereas aniline with a molecular radius of 1·71 is miscible with water in all proportions above 167°, the corresponding critical temperature of aqueous-nitrobenzene mixtures is 235° (Campetti and Delgrosso, *Mem. R. Accad. Sci., Torino*, 1911, [ii], **61**, 187). On the other hand, although both liquids are only partly miscible with the petroleum fraction at 15°, nitrobenzene is relatively more soluble than aniline and is miscible in all proportions at a much lower temperature.

Petroleum–Nitrobenzene–Glycerol Mixture.

The complexity of the glycerol molecule has been ascertained to be one-fourth of that of water, and its molecular volume in the liquid state is only slightly greater in magnitude (*loc. cit.*). The difference, however, is sufficiently great to result in glycerol and aniline being miscible in all proportions at ordinary temperatures. Nitrobenzene, with a greater molecular volume than aniline, is

only partly miscible with glycerol, so that a three-layer system is readily obtained with equal volumes of petroleum, nitrobenzene, and glycerol. At 5°, the approximate proportions of the layers

are
Petroleum layer 23
Nitrobenzene layer 42, the nitrobenzene taking the inter-
Glycerol layer 35

mediate position between the petroleum and glycerol. At temperatures above 17°, two layers only are formed, due to the nitrobenzene dissolving in the petroleum.

As already stated, these investigations were of a preliminary nature, their object being to provide data for subsequent determinations of the equilibrium existing in three-layer systems of liquids. The work here described was brought to a close in 1915, and as an early return to it does not seem probable, it was thought desirable to place on record such results as had been obtained.

In conclusion, I desire to express my indebtedness to Sir J. J. Dobbie, M.A., LL.D., F.R.S., for facilities afforded me in carrying on these investigations.

THE GOVERNMENT LABORATORY.

[*Received, March 8th,* 1918.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 21ST, 1918, AT 4.30 P.M.

Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

The PRESIDENT announced that Professor Gilbert Thomas Morgan had been nominated by a number of Fellows as a Vice-President, in the place of Lt.-Col. Arthur Smithells.

Dr. A. J. EWINS and Professor A. G. GREEN were elected Scrutators, and the ballot was opened for the election of Officers and Council.

On the motion of Professor H. E. ARMSTRONG, the meeting agreed that the Report of Council, 1917–1918, should be taken as read. The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending December 31st, 1917, was proposed by Sir HERBERT JACKSON, seconded by Dr. A. E. H. TUTTON, and carried.

REPORT OF COUNCIL, 1917—1918.

The Council are gratified to report a substantial increase in the number of Fellows during the past year. On December 31st, 1916, the number of Fellows was 3,198. During 1917, 162 Fellows were elected and 10 reinstated, making a gross total of 3,370. The Society has lost 39 Fellows by death, 14 have resigned, the elections of two have been declared void, and 45 have been removed under the action of Bye-law IV for non-payment of annual subscriptions. The net total number of Fellows, therefore, as at December 31st, 1917, was 3,270, showing an increase of 72. During 1916 there was a decrease in membership of 5.

It is with profound regret they report that the following have either been killed or have died of wounds received in action :—

Arthur Joseph Brearley (1913).
Bertram Haward Buttle (1910).
Norman Phillips Campbell (1913).
Edward William Lanchester Foxell (1907).
John Maxwell Heron (1908).
Maurice Kemp-Welch (1903).
Herbert King (1897).
Arthur Edwin Tate (1909).

and that the following Fellows have died :—

Andrea Angel (1905).
James Hector Barnes (1905).
William Thirlwall Bayne (1879).
Clayton Beadle (1891).
John Forbes Bell (1907).
Charles Bradshaw (1888).
George Carrington Carrington (1887).
Alexander Macomb Chance (1883).
Taylor Cook (1907).
George Stanley Cooper (1915).
John Kent Crow (1880).
William Ralph Dodd (1886).
Oliver Statham Douse (1911).
John Joseph Eastick (1881).
John Kerr Forrest (1904).
Reginald Le Neve Foster (1872).
Ernest George Hill (1896).
George Thomas Holloway (1886).
Peter MacEwan (1886).
Norman Harry John Miller (1885).
Benjamin Horatio Paul (1868).
Rufus Daniell Pullar (1882).
John Ffraid Richardson (1911).
Henry Charles Stewart-Carlile (1917).
Francis Sutton (1860).
William Henry Symons (1874).
Walter Arthur Voss (1889).
Thomas Utrick Walton (1884).
John Williams (1892).
Charles Henry Wood (1860).
Philip John Worsley (1858).

Resignations have been received from :—

Edward James Caley (1894).
Arthur Carey (1892).
Patrick Carmody (1889).
Tom Peach Colclough (1912).
Walter Bromley Cooley (1888).
Ridsdale Ellis (1912).
Alfred William Gerrard (1875).
Harry Sands Grindley (1906).
Edwin Reginald Hughes (1903).
Norton Henry Humphrys (1883).
Stanley Allen Warrington Okell (1908)
Frederick Alfred Pickworth (1913).
Alfred Oswald Ransome (1910).
William Frothingham Roach (1908).

The hearty congratulations of the Society are offered to Sir William Crookes, Past President, elected a Fellow on December 3rd, 1857, and to Mr. John Frederick Davis, elected December 17th, 1857, who have now been Fellows for over 60 years, and also to the following who have attained their jubilee as Fellows :—

	Elected.
Sir William Phipson Beale, Bart.	Dec. 5, 1867.
Professor Alexander Crum Brown............	Dec. 5, 1867.
Mr. Facundo Joaquin Ramon Carulla	Dec. 5, 1867.
Professor Georg Lunge	Dec. 5, 1867.
Mr. Robert Rattray Tatlock	Dec. 5, 1867.
Professor Herbert McLeod	Feb. 6, 1868.

The volume of Transactions for 1917 contains 1,128 pages, of which 960 pages are occupied by 95 memoirs, the remaining 168

pages being devoted to the Obituary Notices, two lectures on special subjects, the report of the Annual General Meeting, the Presidential Address, and the Table of International Atomic Weights. The volume for the preceding year contained 103 Memoirs occupying 1,212 pages. The Journal for 1917 contains also 2,858 abstracts occupying 1,308 pages, whilst the abstracts for 1916 numbered 3,281 and occupied 1,532 pages. The diminution in the output of chemical memoirs referred to in the last report, continued throughout the year and apparently will be still more marked in the present year. It has still been possible to obtain most of the continental journals for abstraction, and, considering the circumstances, with but little delay.

The abstracts may be classified as follows :—

PART I.	Pages.	No. of Abstracts
Organic Chemistry	—	886
Physiological Chemistry	—	265
Chemistry of Vegetable Physiology and Agriculture	—	246
	724	1,397
PART II.		
General and Physical Chemistry	—	539
Inorganic Chemistry	—	290
Mineralogical Chemistry	—	90
Analytical Chemistry	—	542
	584	1,461
Total in Parts I and II	1,308	2,858

The Council has decided to award the Longstaff Medal for 1918 to Lieut.-Col. Arthur W. Crossley, C.M.G., F.R.S.

During the past year a Joint Committee, comprising representatives of the Chemical Society and the Society of Chemical Industry, has thoroughly explored the possibility of the co-operation of the two Societies in the preparation and publication of abstracts. The Council are glad to report that, as the result of the labours of the Committee, arrangements are now in force which will practically eliminate the overlap hitherto existing in the two sets of abstracts. The editors of the Journals are in touch with one another, and the periodicals coming under review for abstracting purposes are allocated according to an agreed plan.

The economies effected by this scheme of collaboration should be considerable, but still more important, in the view of the Council, is the fact that a beginning has been made in the consolidation of

the interests of the two Societies concerned. The Council feel confident that, especially from this point of view, the new arrangements will be heartily welcomed by the Fellows of the Society. It is earnestly hoped that further developments along the same lines may be found possible, and in particular that, by the joint efforts of the two Societies, the scope of the chemical abstracts published in this country may be extended, and their value correspondingly enhanced.

The two Councils have further given their provisional approval to a scheme whereby the abstracts of each Society would be obtainable, separately and at a reasonable cost, by the members of the other Society. Steps have been taken to ascertain the amount of support likely to be given to this arrangement.

In connection with the Annual Reports, it has been decided to postpone the one dealing with the progress made in Radioactivity during the year 1917 and to publish in 1919 a combined Report for 1917 and 1918. The title of the Branch "Mineralogical Chemistry" has now been changed to "Crystallography and Mineralogy," and in accordance with the announcement made last year, the Report on this Branch appearing in Volume XIV of the Annual Reports covers the years 1916 and 1917.

For the reasons stated in the letter from Sir Edward Thorpe appearing in the Transactions for 1917 (p. 1001), it was decided to reprint the Table of Atomic Weights published in 1916. Dr. Alexander Scott, Sir Edward Thorpe and Sir William A. Tilden have been appointed by the Council to form a Committee to consider and report on a scheme for the future publication of International Atomic Weights.

The usual List of Fellows was not published in 1917 owing to the necessity of economy in the use of paper; but although this is still urgent, it has been considered desirable not to postpone publication for another year.

In view of the smaller number of scientific communications which are available for reading to the Society, the Council have decided that during the present Session the proceedings at three Ordinary Meetings shall be limited to purely formal business, and that on each occasion an Informal Meeting shall immediately follow. By arranging that an Informal Meeting should take place in the evening after the Annual General Meeting, the Council hope to afford added opportunity for personal intercourse among Fellows.

Three Lectures have been arranged for the session 1917–1918. The first of these was given on December 6th by Dr. Frank L. Pyman, who lectured on "The Relation between Chemical Constitution and

Physiological Action," whilst on February 21st Professor the Hon. R. J. Strutt delivered his Lecture entitled "Recent Studies on Active Nitrogen." The Council are pleased to announce that Dr. Horace T. Brown will deliver his Lecture, "The Principles of Diffusion; their Analogies and Applications," on June 6th next. This Lecture was to have been delivered in March, 1917, but was unfortunately postponed owing to illness of the lecturer.

Fellows will remember that one of the conditions accepted by the Council in receiving the gift of £1,000 to the Research Fund from Mrs. and Miss Müller was that a lecture dealing with the relationship between Chemistry and either Botany or Mineralogy should be delivered once in every three years. The first of these Lectures, to be known as the Hugo Müller Lectures, will be given on April 18th by Sir Henry Miers, who will discourse on "The Old and the New Mineralogy."

The situation created by the orders calling up for military service all men between the ages of 18 and 22, with the exception of engineers, was referred by the Council to the General Committee of Chemical and Allied Societies, who passed the following Resolution:—

> "This Committee desires to associate itself with the Royal Society in their action concerning the calling up of Chemists holding exemption on the recommendation of the Royal Society, and would be glad to take any action which the Royal Society consider would strengthen their hands in the matter."

This resolution was forwarded to the Royal Society. The Council also addressed communications to the War Office and other Government Departments pointing out that chemists were essential to the present and future welfare of the country, and that it would be a mistaken policy to remove them from their present occupations. The General Committee also have before them the question of hastening the release of chemists from the Colours on the cessation of hostilities.

The opinion of the Council on the proposed publication of Chemical Bibliographies in the English language has been requested by a Provisional Committee dealing with this question. The Council, deeming this to be a matter on which the Chemical and Allied Societies should confer, have referred it to the General Committee.

The problem of increasing the use and scope of the Library,

more particularly on the technical side, is engaging the attention of the Council, and the matter has been referred to a Conference of the Representatives of Chemical and Allied Societies for consideration and report. It is hoped that the results of these several deliberations will be issued to Fellows in the near future.

The congratulations of The Chemical Society have been conveyed to Professor S. Hoogewerff, of The Hague, on his attaining his 70th birthday.

Professor Percy F. Frankland and Dr. Alexander Scott have again been appointed to represent the Society on the Board of Scientific Societies.

Sir William A. Tilden has accepted the invitation of the Council to represent the Society on the Court of the University of Bristol.

The number of books borrowed from the Library during 1917 was 2157, as against 1610 the previous year. The additions to the Library comprise 155 books, of which 62 were presented, 282 volumes of periodicals and 54 pamphlets, compared with 115 books, 329 volumes of periodicals and 35 pamphlets in 1916.

The accounts for the year 1917 show a balance of income over expenditure amounting to £1,652 9*s*. 11*d*. as against £1,865 19*s*. 9*d*. reported last March for the previous year. Whilst the income from all sources was £8,529 18*s*. 11*d*., and therefore greater than that for 1916 by £365 19*s*. 1*d*., the expenditure exceeded that of 1916 by £579 8*s*. 11*d*., and reached the sum of £6,877 9*s*. 0*d*. This increase in expenditure is due principally to enhanced cost of producing the various publications, expenses on account of the Journal being £4,420 19*s*. 2*d*. as against £4,074 14*s*. 0*d*. during 1916, whilst the Annual Reports cost £64 14*s*. 2*d*. more than in the previous year. Various items of administrative expenditure have brought the aggregate under this heading from £1,281 5*s*. 11*d*. to £1,472 4*s*. 5*d*., including an increase from 15 per cent. to 20 per cent. in the war bonus paid to the staff, the provision of library furniture and of a larger supply of stationery; it has also become necessary to extend the insurance policy from £12,000 to £14,500.

The compensating items of increased income are £82 10*s*. 0*d*. on account of subscriptions, £135 11*s*. 0*d*. from interest on investments, £100 17*s*. 6*d*. from the sale of publications, and £86 9*s*. 5*d*. from advertisements in the Journal, the improved dividend on the Society's capital being principally due to the purchase of War Loan with the balance from 1916.

In the Reports for the last two years it has been the practice

to indicate the effect of the War upon the size of the Journal, and this may be brought to date by the following synopsis :—

	Number of Pages.		
	Trans.	Abstr.	Total.
1914..............	2,909	2,068	4,977
1915..............	1,862	1,944	3,806
1916..............	1,368	1,532	2,900
1917..............	1,128	1,308	2,436

It thus appears that the Journal has diminished to just under one-half the pre-war standard, and it is disturbing to find that whilst the cost of printing was £3,230 6*s.* 6*d.* in 1914, the corresponding expenditure for 1917 has been £2,543 7*s.* 9*d.*, an increase of more than 50 per cent. having regard to the relative number of pages concerned. This appreciation is due to the greatly increased cost of paper and to the fact that it has been found necessary to augment the bonus paid to Messrs. Richard Clay and Sons, Limited, which is now 37½ per cent. Valuable assistance has been rendered to the Society, however, by Mr. C. F. Cross, who has recently secured an improvement in the quality of the paper upon which the Journal is printed and has advised the Council in respect of the price which should be paid for it.

One grant only has been made from the Research Fund during 1917, the disbursement being one of £10 as against £94 for 1916, £137 for 1915, and £287 for 1914. Repayments have amounted to £61, and as the dividends have increased by £73, the excess of income over expenditure amounts to £553 2*s.* 0*d.* as against £380 17*s.* 9*d.* for 1916. Early in 1917, £500 War Loan 5 per cent. Stock was purchased with the balance from the previous year, and this capital sum, together with the substantial investment recorded in the previous Report, will help to provide a considerably increased annual amount to be expended upon chemical research when circumstances permit the resumption of normal activities.

A vote of thanks to the Auditors was proposed by the Treasurer and seconded by Dr. G. Senter, Dr. C. A. Keane making acknowledgment.

Professor W. A. Bone proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. This was seconded by Dr. H. Forster Morley and acknowledged by Mr. A. Chaston Chapman.

In presenting the Longstaff Medal to Lt.-Col. Arthur W. Crossley, the President said:

"The introduction of ethyl malonate and ethyl acetoacetate as synthetic agents for the preparation of polymethylene derivatives

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st December, 1917.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance	139	3	4			
	3	0	0			
				142	3	4
,, Sundry Creditors				723	0	7
,, Research Fund:—						
As per last Balance Sheet	13804	1	4			
Add Excess of Income over Expenditure for the year	553	2	0			
				14357	3	4
,, Chemical Society: Excess of Assets over Liabilities:—						
As per last Balance Sheet...	23105	17	6			
Add Excess of Income over Expenditure for the year	1652	9	11			
				24758	7	5
				£39980	14	

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£6730 Metropolitan Consolidated $3\frac{1}{2}$ per cent. Stock	7212	8	6			
£1050 London and North Western Railway 3 per cent. Debenture Stock	839	12	0			
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India $2\frac{1}{2}$ per cent. Stock	1316	1	0			
£2400 Bristol Corporation $2\frac{1}{2}$ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway $2\frac{1}{2}$ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Debenture Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	1460	13	6			
£1200 North British Railway 3 per cent. Debenture Stock	1033	11	0			
£700 Canada $3\frac{1}{2}$ per cent. Stock, 1930/50	704	8	6			
£2100 5 per cent. War Stock } £1100 5 per cent. War Bonds }	3040	0	2			
(Estimated present value of Investments, £16832 2*s.* 6*d.*)				24042	0	1
,, Sundry Debtors				861	18	2
,, Subscriptions in Arrear Estimated to realise...				400	0	0
,, Insurance paid in advance				68	13	4
,, Cash at Bank—Deposit Account	500	0	0			
Less Current Account, overdrawn	271	3	2			
	228	16	10			
,, Cash in hand	22	2	11			
				250	19	9
,, Research Fund:—						
Investments (value when acquired):						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated $3\frac{1}{2}$ per cent. Stock	4587	18	0			
£1034 Great Western Railway $2\frac{1}{2}$ per cent. Debenture Stock	1049	15	11			
£1142 16*s.* New South Wales 3 per cent. Stock ...	1000	0	0			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9			
£1365 Midland Railway $2\frac{1}{2}$ per cent. Debenture Stock	1010	0	9			
£806 Victoria 3 per cent. Stock	706	6	2			
£3681 11*s.* 3*d.* 5 per cent. War Stock	3497	10	1			
				13864	7	8
(Estimated present value of Research Fund Investments, £10977 5*s.*)						
,, Cash at Bank...				492	15	8
				£39980	14	8

INCOME AND EXPENDITURE ACCOUNT

Income.

	£ s. d.	£ s. d.
To Life Compositions ...		247 0 0
,, Admission Fees ...		604 0 0
,, Annual Subscriptions—		
Received in advance, on account of 1917 ...	250 0 0	
,, during 1917 ,, ,, ...	4341 0 0	
,, ,, ,, ,, 1916 ...	366 0 0	
,, ,, ,, ,, 1915 and previous ...	36 0 0	
	4993 0 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet ...	390 0 0	
	4603 0 0	
Add Arrears at date: 1917, £504; 1916 and previous, £554, estimated to realise as per Balance Sheet ...	400 0 0	5003 0 0
,, Lady Subscribers ...		7 10 0
,, Investments:—		
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...	176 13 4	
,, £1050 London and North Western Railway 3 per cent. Debenture Stock ...	23 12 6	
,, £1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock ...	34 4 4	
,, £1400 India 2½ per cent. Stock ...	26 5 0	
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock	45 0 0	
,, £4341 Midland Railway 2½ per cent. Preference Stock	82 15 0	
,, £1200 Leeds Corporation 3 per cent. Debenture Stock...	27 0 0	
,, £1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	33 15 0	
,, £1200 North British Railway 3 per cent. Debenture Stock ...	27 0 0	
,, £700 Canada 3½ per cent. Stock 1930/50 ...	19 13 9	
,, £3200 5 per cent. War Stock and War Bonds...	122 11 3	
,, Income Tax Recovered ...	135 8 11	
,, Interest on Deposit Account ...	36 16 4	790 15 5
,, Publication Sales:—		
Journals ...	1485 19 0	
Proceedings ...	10 5 0	
Collective Index ...	54 7 5	
Library Catalogue ...	1 0 0	
Atomic Weight Tables ...	5 9	
Annual Reports on Progress of Chemistry ...	170 18 0	
Memorial Lectures ...	3 3 3	
	1725 18 5	
Less Publishers' Commission ...	167 13 2	1558 5 3
,, Proceeds of Advertisements in Journal...	£308 6 3	
Less Commission ...	27 2 6	281 3 9
,, Miscellaneous Receipts ...		4 2 0
,, Subscriptions from other Societies ...		34 2 6
		£8529 18 11

I have examined the above Accounts with the Books and Vouchers of the Society, and the Investments.

23, Queen Victoria Street, E.C. 4.
March 4th, 1918.

W. B. KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1917.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal :—		
Salary of Editor, including Indexing ...	620 0 0	
Salary of Sub-Editor and Assistant ...	250 0 0	
Editorial Postages ...	16 15 1	
Abstractors' Fees ...	308 12 2	
Printing of Journal ...	2543 7 9	
Banding ...	56 6 11	
Printing of Advertisements ...	104 2 7	
Wrappers and Addressing ...	4 9 9	
Distribution of Journal ...	401 2 9	
Authors' Copies ...	97 0 0	
Insurance of Stock ...	19 2 2	
		4420 19 2
,, Annual Reports on the Progress of Chemistry ...		435 13 0
,, Purchase of back numbers of Journal ...		5 18 6
,, Library Expenses :—		
Salary of Librarian and Assistant...	269 18 0	
Books and Periodicals ...	193 10 2	
Binding ...	39 5 9	
		502 13 11
,, Indexing for International Catalogue ...		0 0 0
,, Donation to International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological ...		10 0 0
,, Administrative Expenses :—		
Salary of Staff ...	430 15 0	
War Bonus ...	201 11 9	
Wages (Commissionaire, Housekeeper, and Charwoman) ...	187 16 6	
Coal and Lighting ...	72 15 2	
House Expenses and Repairs ...	96 4 5	
Furniture ...	69 12 9	
Tea Expenses ...	27 3 6	
Insurances ...	32 0 6	
Accountants' Charges ...	21 0 0	
Commission on Recovery of Income Tax ...	6 15 5	
Law Costs ...	1 1 0	
Miscellaneous Printing ...	84 5 7	
Stationery ...	117 5 1	
Postages ...	77 12 2	
Miscellaneous Expenses ...	46 5 7	
		1472 4 5
,, Balance, being excess of Income over Expenditure carried to Balance Sheet ...		1652 9 11
		£8529 18 11

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved—CHARLES A. KEANE,
E. W. VOELCKER,
C. F. CROSS.

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1917.

Income.

	£ s. d.	£ s. d.
To Dividends on:—		
£1000 North British Railway 4 per cent. No. 1 Preference Stock	30 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock ...	115 10 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	19 7 8	
£1142 16*s*. New South Wales 3 per cent. Stock...	25 14 4	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	25 5 0	
£1365 Midland Railway 2½ per cent. Debenture Stock ...	25 11 10	
£806 Victoria 3 per cent. Stock	18 2 8	
£3681 11*s*. 3*d*. 5 per cent. War Loan	159 4 6	
		418 16 0
(£418 8*s*. 6*d*. purchased during year 1917)		
Repayments of Research Grants		61 1 10
,, Income Tax Recovered		92 19 8
		£572 17 6

Expenditure.

	£ s. d.
By Grant to H. Wren	10 0 0
,, Cheque Book	8 0
,, Commission on Recovery of Income Tax	4 13 0
,, Advertisements	4 14 6
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet	553 2 0
	£572 17 6

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23, QUEEN VICTORIA STREET, E.C.
March 4th, 1918.

Approved—CHARLES A. KEANE,
E. W. VOELCKER,
C. F. CROSS.

heralded an entirely new aspect of organic chemistry. Until some thirty years ago, almost the only closed-chain compounds which had been fundamentally studied were derived from the aromatic hydrocarbons, and the well-recognised stability of the benzene ring had led to the development of a quite specific kind of technique—a technique in which a certain roughness in chemical treatment was permissible. The investigation of the polymethylene derivatives soon showed that these substances called for much more delicate handling.

"Professor Crossley is well known to us as one of the most assiduous workers in this new field. He has contributed to the Society a large number of papers, more especially on dihydrobenzene and hexamethylene derivatives, all of which show evidence of masterly experimentation, and many of which have important bearings on the constitutions of camphor and other components of the essential oils. Much of his earlier work was carried out under conditions which left something to be desired as regards laboratory accommodation and general facilities; British chemistry owes much to men who, like Professor Crossley, have persevered and succeeded, no matter how unfavourable to original work were the conditions under which they were placed in their earlier days.

"Professor Crossley, it affords me great pleasure, in the name of the Council, to hand you the Longstaff medal for original research in chemistry. We hope that the important work upon which you are now engaged will come to an end at no distant date, and that you will then return with fresh vigour to your life-work in the service of our science."

The PRESIDENT then delivered his Address, entitled, "The Future of Pure and Applied Chemistry." Professor H. E. ARMSTRONG moved a vote of thanks to the President for his services in the Chair during the past year and for his Address, coupled with the request that he would allow the Address to be printed in the Transactions. He also expressed the hope that the Council would circulate it among both Houses of Legislature. The motion was seconded by Professor W. H. PERKIN and carried with acclamation, the PRESIDENT making acknowledgment.

The report of the Scrutators was presented, and the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year:

President.—William Jackson Pope, C.B.E., M.A., D.Sc., F.R.S.

Vice-Presidents who have filled the Office of President.—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc.,

F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; William Odling, M.A., M.B., F.R.S.; William Henry Perkin, Sc.D., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; Alexander Scott, M.A., D.Sc., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., LL.D., F.R.S.

Vice-Presidents.—Frederick George Donnan, M.A., Ph.D., F.R.S.; George Gerald Henderson, M.A., D.Sc., F.R.S.; Arthur Lapworth, D.Sc., F.R.S.; Arthur Smithells, B.Sc., F.R.S.; William Palmer Wynne, D.Sc., F.R.S.; Sydney Young, D.Sc., F.R.S.

Treasurer.—Martin Onslow Forster, D.Sc., Ph.D., F.R.S.

Secretaries.—Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

Foreign Secretary.—Arthur William Crossley, C.M.G., D.Sc., F.R.S.

Ordinary Members of Council.—Julian Levett Baker; Alfred Chaston Chapman; David Leonard Chapman, M.A., F.R.S.; Alexander Findlay, M.A., D.Sc., Ph.D.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Anderson Henry, D.Sc.; Charles Alexander Hill, B.Sc.; James Colquhoun Irvine, D.Sc., Ph.D.; Sir Herbert Jackson, K.B.E., F.R.S.; Robert Howson Pickard, D.Sc., Ph.D., F.R.S.; Frank Lee Pyman, D.Sc., Ph.D.; Edward William Voelcker.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 21st, 1918.

By WILLIAM JACKSON POPE, C.B.E., M.A., D.Sc., LL.D., F.R.S.

The Future of Pure and Applied Chemistry.

ONE of the most pleasurable events of annual recurrence during my younger days was the Presidential Address to the Chemical Society; it was generally a carefully prepared discourse on some technical subject of which the author was a master, and always left a lasting impression on the mind of the apprentice to our science. The long list of past Presidential addresses to our Society constitutes a maturely reasoned history of the development of chemistry during the last seventy years.

For three years past pure chemical research has been dormant the whole world over, and it would be difficult for the most accomplished essayist to arrest your attention for an hour by an address on a subject of purely academic interest. Our mental point of view and our outlook upon both present and future are entirely different from those of four years ago; although the present is obscure and painful, the future gives promise of brilliant and rapid developments in natural science in general and in chemistry in particular. In this belief I venture to lay before you some reflections upon the growing recognition of the importance of our science and upon the responsibilities with which, owing to this change in public opinion, our shoulders are laden.

I have often heard the statement made by men who have grown old in the service of science that chemistry, and particularly applied organic chemistry, is a subject in which the British nation can never excel: that minute attention to detail, coupled with the power of organisation and co-operation, entails something antipathetic to the British character; the Germans, we know, have often expressed this view. The events of the last three years have sufficed to dissipate this fallacy for ever. The manner in which Great Britain, caught in the autumn of 1914 with scarcely any resources in the shape of equipment for the manufacture of fine organic chemicals, has rapidly become a larger producer of explosive, pharmaceutical, photographic, and other essential chemicals

than Germany, will remain an enigma to the historian of these present times. The obscurity which surrounds this rapidly executed operation is not diminished by the existence of difficulties which have naturally acted as inhibiting agents. This country enjoys in a greater measure than any other State a representative Government; in spite of the many advantages of such a form of Government, the fact remains that it necessarily admits of no representation of any phase of public opinion which is not loudly and insistently expressed. Science has always been in this latter position; it has been unvocative. During the first few years of the nineteenth century, Dalton enunciated the atomic theory, Thomas Young stated the undulatory theory of light, and James Watt invented the steam engine, and by these events all the amenities of human life have been revolutionised; indeed, they have exercised vastly more influence on the well-being of our race than did the Napoleonic wars. So accustomed are we, however, to routine habits of thought that most of us would probably answer, in reply to a suddenly posed question, that the battle of Trafalgar was the most pregnant event of the first quarter of the nineteenth century.

A brief moment of reflection would lead us to correct this hasty statement. Sodium was discovered by Davy in 1807, and benzene by Faraday in 1823. From sodium we obtain sodamide, the prime agent in making artificial indigo an economic possibility; the separation of benzene from coal-tar led by logical sequence to the production of Perkin's mauve and of thousands of other synthetic colouring matters, and to the manufacture from coal-tar anthracene of synthetic alizarin, the first heavy blow aimed at the position of the Turkish Empire, involving as it did the ruin of the Turkey-red or madder industry. The first practical process for making aluminium depended on the use of Davy's sodium, and with the aid of Davy's safety lamp 250,000,000 tons of coal are mined annually in this country with comparatively slight risk. Faraday's early investigations on the chemical aspects of electrolysis and his studies on magnetic induction led immediately to the invention of the dynamo, and, through Clerk Maxwell, to the introduction of wireless telegraphy; this one branch of Faraday's investigations, in point of fact, constitutes the ground-work of the whole stupendous vista of results of the general introduction of the electric current into modern life which is so familiar to us all. Cavendish's early production of nitric acid by the passage of an electric spark through air, reproduced on an enormously larger scale, is now furnishing Central Europe with the nitric acid without which no explosives could be manufactured.

The above-mentioned and multitudes of other fundamental dis-

coveries in physical and chemical science were made almost within a stone's-throw of this room; most of them were made in the Royal Institution, and all of them by an expenditure of money infinitely small as compared with their present-day effects.

Anyone who is in the habit of reading modern historical writers —and they have become quite illuminating since a scientific mode of writing history has been substituted for the older fictional style —knows how political changes, national reforms arising from an effort of the collective conscience, the magnetic influence of some popular demagogue, and the like, are invariably invoked as explanatory of all the vicissitudes of our planet.

The modern historian is here taking a false point of view, and, since he is, in general, quite unacquainted with physical science, his methods are inadequate. The whole history of Europe for the last century has been made within a few hundred yards of Burlington House in our scientific laboratories. One of the most potent incentives to political changes resides in the desire to increase the amenities of life, and research in pure science has had for a hundred years past the greatest influence in facilitating the realisation of that desire. Co-operative effort, one of the most striking aspects of modern life, only became possible when science provided the facilities for municipal power schemes, for telegraphic connexion over the whole world, and for the concentration of production in definite centres. Chemical science is still furnishing the means for further revolutionary changes; during the last few years we have seen great technical developments of purely scientific discoveries—the work of Dewar on the liquefaction of gases, and that of Cross and Bevan on viscose and artificial silk, both of which have led to the profitable utilisation of vast amounts of capital—and it is as yet impossible to indicate the ameliorations of the conditions of human life which will inevitably result from contemporary chemical investigation.

In a time of crisis like the present, British custom tends towards the replacement of unreal conventions by what is really vital; we have been engaged upon this operation for several years. Whilst previously unheard-of changes have succeeded each other kaleidoscopically in the national constitution, in the political parties in power, in the freedom of the subject, and in hosts of other ways, the nation has recognised that science is the only real maker of history. The whole Empire is now one vast chemical and engineering laboratory, and we even live on a scientific ration of so many calorific units. It is obvious that chemistry, with physics, engineering, preventive medicine, and others of the natural sciences, which previously had no imperialistic position, because powerless

to make or break a Government, have become the pivot on which turn all our hopes of retaining an independent national existence; it has been suddenly realised that supremacy in these branches of knowledge is vital to our country.

The time is approaching when this state of affairs will change; neglect of the natural sciences will then no longer put us in danger of sudden extinction, but, as was taking place years ago, will lead to our slow, certain downfall as a nation. The responsibility is placed upon our scientific men of taking such measures as will ensure that the old order is not re-established, that science makes her voice heard in our national councils, and that policies of drift are for ever abandoned.

We have in this country three large and long-established organisations devoted to various phases of chemical science: the Chemical Society, the Society of Chemical Industry, and the Institute of Chemistry. Is it too much to ask that these three representative bodies, with perhaps the newly-founded Association of British Chemical Manufacturers, and ultimately all the other cognate but more specialised interests, should set up a watchful and alert joint Council with directions to consider national questions in which any of the varied interests of chemistry are concerned, and to make such representations to our administrators as would voice the corporate view of the joint body.

I am inclined to think that, had such a body been in existence several years ago, much that has been accomplished in the interval by somewhat devious methods would have been better done. One instance will occur to everyone: that of the much-debated question of the re-establishment of the coal-tar colour industry in Great Britain. The scheme adopted by the Government for resuscitating this phœnix in our country, after its past thirty years of profligate productivity on the Continent, was launched without scientific advice; the Cabinet mouth-piece, indeed, declared that the directorate of the company was not to include men of scientific knowledge, on the ground that a director who knew something about the business of the company would have an advantage over his less well-informed colleagues.

Owing largely to the fact that we possess no strong collective council, representing the combined academic, scientific, and industrial aspects of our science and capable of representing them before a representative Government, it may be argued that we chemists are not altogether blameless for the particularly blundering way in which particular errors have been perpetrated by the responsible officials. Whilst we should be thankful that our blunders have not led to our destruction, we should proceed without further

delay so to organise the resources of chemistry as to make it possible to enforce the adoption of scientific methods and modes of thought by authorities to whom these are yet strange.

The serious character of the British position in connexion with the coal-tar colour industry becomes more evident when one considers that this is a key industry; upon it depend the textile, paper, photographic, and pharmaceutical industries. The total capital employed in the organic dye industry in Great Britain is between four and five million pounds, whilst the capitalisation of the German coal-tar colour firms is of the order of fifty million pounds. The need for greater and more intelligent activity in this direction is obvious; unless national enterprise can be stimulated into providing adequately for the manifold requirements of Great Britain and her Colonies in all those industries which depend on coal-tar colour manufacture, we shall be again in the hands of the foreign producer.

The control of a national dye scheme by business men with no real feeling for the enterprise on which they are engaged renders it fairly certain that the wider aspects of coal-tar colour manufacture will be neglected. The interweaving of the colour interests with those of synthetic pharmaceutical, photographic, and other chemical industries is essential to success. The utilisation and development of the resources of the Empire in natural colouring matters such as indigo is necessary from a national point of view. The careful study of our own and other codes of Patent Law in their bearings upon the fine chemical industry is also important. These weighty questions cannot receive adequate consideration from any purely lay body.

It is mournful but instructive to compare our present position in the coal-tar colour industry with the prospects which that branch of applied chemistry exhibited to Great Britain in early days. The first coal-tar colour was made by Perkin in 1856, and in 1862 Professor A. W. von Hofmann, one of the foremost chemists of the day, a German, domiciled in this country, painted an alluring picture of the future in store for us. Said he: "England will, beyond question, at no distant day, become herself the greatest colour-producing country in the world, nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, etc." When we contrast this dazzling prospect, made by one of the most far-sighted of contemporary German chemists, with the actual situation, we cannot but ask why the event fell so miserably behind the forecast. The reason, in my opinion, lies in the fact that opulent, indolent Great Britain has

for the past century permitted all its educational interests to pass into the hands of a particular caste which despises all knowledge difficult to attain and, to camouflage its own idleness, has always pressed the notion that a first-hand knowledge of the facts of natural science and the conclusions to be drawn therefrom is unimportant, and that the young man or young woman does his or her best in the world if thrown into it entirely destitute of anything but an evanescent acquaintance with certain classics and a decided taste for so-called learned leisure. The greater among the ancients were creators of new knowledge as well as masters of the whole accumulated world's stock of information; their successors, unproductive of positive knowledge and very ignorant of the great changes taking place around them, can but wonder at and comment vaguely on the genius of Archimedes and Aristotle, and necessarily despise the achievements of Newton and Kelvin, their modern prototypes. Illustrations of the stultifying effect of a purely classical education are laid before us every day; one recent example may be quoted here. The gentleman who shares with Mr. A. J. Balfour the honour of representing in Parliament the greatest centre of business and financial activity in the world made the following statement in the House of Commons last Thursday whilst opposing Mr. Fisher's Education Bill: "It was said that education was necessary to make the rising generation good business men. His experience in the City was that the man who took Firsts at Oxford generally came out last, and that the man who could hardly write his name generally came out first. The explanation was that education could not put into a man that instinct of self-preservation and common sense which was the foundation of all success in business. How could education assist a farm labourer to spread manure on a field? The best labourer he had known was wholly illiterate. If the waste of the war was to be replaced it would be necessary for the young to start as early as possible in doing a day's work, instead of wasting time on useless book learning." This representative of the City of London is a baronet of recent creation and a director of one of the largest London banks and of one of the most important English railroads; he received his "education" at one of the oldest and most rigidly classical of our great public schools. Comment is probably unnecessary.

Every scientific man in the world realises that an innate appreciation for fine literature, for great thoughts nobly expressed, and for the appropriate delineation of our greatest aspirations, are among the most sublime instincts of humanity and demand the most careful cultivation. Our literary men say that we cannot

express ourselves effectively, and offer as a satisfying feast the old bones left us by the Greeks and Latins, chewed over for centuries until so devoid of nutriment that they led ultimately to the mental atrophy which characterised the Middle Ages, an atrophy that was only shaken off by the taste for knowledge which arose from the exploits of geographical science in the Elizabethan period.

If the power of expression rests with our literary friends, why are they so idle? It is their obvious duty to devote themselves to popularising the natural knowledge acquired by the scientific observers of the past two centuries; this real learning has so infinitely extended human interest in the world around us and gives such promise of further conquests that an appeal for its consideration would certainly not have been made in vain to Plato or Lucretius. No one asks for the abolition of classical literary learning, but the whole world is now demanding that the young should be provided with an education which includes an insight into our present-day knowledge of the universe.

The rather petty disputes which rage about this matter of classical and scientific education are one-sided; the scientific man generally knows something of both aspects of the subject, whilst his classical compeer rarely has any acquaintance with science. Unfortunately, the great questions involved have more than a petty bearing upon the well-being of our nation. The classical school has held our country in such bondage that, to all practical intent, no person can be admitted to the higher public service unless he swear adhesion to the caste. It is almost regarded as a platitude that acquaintance with natural science disables a man from fulfilling any high public office; practically all the superior positions in the Civil and Diplomatic Services must be filled by men of classical instincts.

I venture to think that the wisdom of this mode of selection has been seriously impugned during the last four years. The huge Government departments which have arisen of late may be divided roughly into two classes—those staffed by men of some scientific training and those staffed by classical university graduates. Anyone who has had occasion to note the numerous recent criticisms on Government departments must have observed that these strictures have almost invariably been passed on administrative branches of the service; delay, the encumbrance of red-tape and inability to draw a decision, seem indigenous in certain Government offices, and none of the numerous attempts at reform has been successful. The administrative services are those in which the classical man is predominant. Other branches, such as the home Army Medical Service, have practically never been charged

with inefficiency; the worst that has been alleged is a suggestion of extravagance.

The department just named is staffed by men who have had, at least, the rudiments of a scientific education; if control in the Royal Army Medical Service had been vested in the classical scholar of ability but no knowledge, it is certain that the last three years would have seen a repetition of the horrors of the Crimean campaign and that the army mortality from disease would have been greater than that caused by the ordinary instruments of war.

Such a control, happily, has been avoided; it has been avoided merely because medicine possesses the collective organisation for which I plead in chemistry, an organisation so strong as to make the imposition of an irresponsible lay control unthinkable.

I have already directed attention to the frequently expressed opinion that, as a nation, we are incapable of excelling in the fine organic chemical industry; let me quote one instance, small in itself, but large in its consequences, in disproof of this view.

The ordinary photographic plate is sensitive only to a region in the blue of the spectrum, but by incorporating certain rather fugitive organic dyes with the sensitive film, the latter may be rendered sensitive to the green, yellow, and red parts of the spectrum; photographic plates so treated are described as panchromatic. The quantities of the sensitising dyes required for the whole world's consumption in normal times is minute, being, indeed, of the order of a few pounds per annum. Until 1915, these substances had never been made outside Central Europe, and little was known by us of their compositions or of the methods of preparing them, as they were all sold under trade names. The manufacture of these materials, small as was the whole business, had been industriously cultivated by the German colour works, and, as these colour sensitisers are essential in aerial photography, their scarcity became of serious import quite early in the war.

The experimental investigation of the whole subject was quickly put in hand in this country, and within a few months ample supplies of the usual sensitisers were produced. Further, the newly established Department of Scientific and Industrial Research financed the development of the study of photographic sensitisers; as a result of this action, new sensitising dyes have been produced which are far superior to the older ones. It is safe to assert that the manufacture of panchromatic plates has now attained a degree of perfection in this country such as will long defy competition.

This is but one case that may be quoted from among a host of others, all of which prove conclusively that, given a little encourage-

ment and assistance, British chemistry is capable, not only of giving much-needed relief in this time of strain, but of meeting every demand which can be made on it when the period of reconstruction commences.

Whilst the absence of the powerful weapon provided by a collective chemical Council, embracing all interests of the science, has made it impossible for us to render the most economical service to our country, it is perhaps satisfactory to reflect that hitherto all that has been sacrificed is economy. Our lack of power to enforce our views has led to financial extravagance on the part of the authorities; the lack of economy in time, which means lives, cannot be attributed to our chemists. The duty will fall to some future President at some later time to record the spontaneity with which the Fellows of this Society volunteered for service in our chemical works, our munition factories, and with the Colours either in our gas service or elsewhere.

One aspect of this question, however, calls loudly for attention. For several years past our teaching staffs have been depleted, and but a small fraction of the normal number of young men have been able to present themselves for training in chemistry. Whilst the present demand for capable young chemists is vastly in excess of the supply, an even more serious situation awaits us in the future. If hostilities were to cease to-morrow, five years would be needed before our colleges and universities could begin to supply the large numbers of young chemists which will be required for the development of the future great fine chemical industry of this country.

Surely this is a matter which should engage the serious attention of the country. If it prove necessary to import young chemists from neutral nations to man our reconstruction schemes a handicap will be established which we may never outrun. The adoption of some scheme by which a sufficient number of juniors can be provided to help in the great developments which the future has in store for the scientific industries of the country is of the utmost importance.

It is impossible to reflect on the desirability of a closer cooperation between the large societies representing chemistry in Great Britain without foreseeing many directions in which such a union would be of value. As in every time of awakening, there exists at present a great feeling of unrest among the younger members of our profession; of late quite a number of propositions for the formation of new scientific societies have been promulgated, and all for the purpose of placing more power in younger hands and for ensuring to the juniors more security of advancement. The final objects of these propositions, so far as I have understood them, are

entirely praiseworthy, but it is to be feared that the methods suggested for their attainment are not always such as appeal to older and more experienced people as likely to prove successful. If we chemists collectively were in possession of some more centralised organisation, such an one, for example, as is represented by the Chemists' Club in New York, with facilities for hospitality, meetings, library, laboratory accommodation, and the like, no question could ever arise of the creation of a new chemical body unconnected with the main organisation. A new and vigorous issue of the parent organisation would shoot at appropriate intervals, and would remain contributing to the strength of the family under the original patriarchal roof. We greatly need a central home of all the chemical interests in the country, and premises several times as large as the Chemical Society rooms, to use as a club, of which every chemist in the country would be a member. The question of the necessary expansion of the Library, which is occupying the earnest attention of your Council, would find an easy solution in such a pooling of interests.

Notwithstanding that, during the past forty years, much has been done to facilitate the entrance of talented and promising young men into the scientific professions, far more progress must be made in this direction if we are to regain for Great Britain the paramount position she once held in scientific discovery. The Natural Science Departments in every University in the country call for expansion in personnel, laboratory space, and equipment, and in provision for post-graduate research work; whilst scholarships for students in training are fairly plentiful, the difficulties which face the advanced student who needs to spend, and who would benefit immensely by spending, several years on original research, are often insurmountable. Every professor of chemistry in the country can recall many instances in which he has had to send his students into technical life at too early a period, simply because it has been impossible to secure for a good man the £150 or £200 per annum necessary for living expenses; the provision of this small sum would, in many cases, convert a half-trained chemist into a far greater asset to the State.

Whilst a collective effort, exerted by all the interested branches of our science, to ensure the efficiency of the newly-established organisations for furnishing the requisite relief, is urgently desirable, it should be noted that it will become increasingly difficult to retain students capable of taking leading positions for a sufficient time to ensure their proper training. During several years past I have been visited by gentlemen representing large chemical industries who have walked round my research labora-

tories to sort out the workers and to make overtures to such as they judged suitable for their own work; the pressure thus exerted upon the universities to force the premature delivery to the works of the best men they have in training will necessarily increase with the coming still greater demand for technical chemists.

The intellectual professions may be roughly classified in two categories: the productive and the parasitic. Those of the productive class, which includes all scientific workers who produce new knowledge, are, in general, poorly remunerated; their practitioners are ordinarily so intensely held by the interest of the work in hand that they have little inclination to divert their energies to the necessary extraction of higher emoluments. The parasitic class, on the other hand, have always been able to command ample remuneration for their labours; the reasons for this difference are various, and need not now be detailed. It may be noted, however, that at the jubilee of this Society in 1891 the veteran, Sir W. R. Grove, who in his young days did so much to develop chemical science, told us that he was led very reluctantly to desert chemistry for the Law because "the necessities of a then large family gradually forced me to follow a more lucrative pursuit." The autobiography of the late Lord Playfair tells a precisely similar tale. Neither of these men is now remembered by anything beyond the great achievements in chemical science of his early days.

The fact emerges that if science is to remain in its service such a proportion of the most powerful intellectual and creative talent of the Empire as will suffice for our progress as a nation, some method must be devised for securing to its followers appropriate emoluments commensurate with those now allocated to the non-productive professions.

This is not only necessary in connexion with those purely utilitarian branches of chemical science to which I have already directed attention, perhaps too insistently, for illustrative purposes. A great danger exists at present, and will grow in the future, that the enormous productiveness of experimental science will overshadow the importance of scientific work of less immediate utility. It would be a great calamity if pure science were neglected in favour of the cultivation only of natural knowledge which gave immediate promise of beneficial material results. One of the most important functions of any expression of collective chemical interests such as I have foreshadowed would be to ensure that pure unproductive scientific research should be retained on an even higher level than that assigned to immediately productive original investigation.

At the present time, physics and chemistry are merging into

one; we foresee that the near future will furnish us with still broader views of the universe and will mark a new development more illuminating even than the great advances which followed Dalton's atomic theory and all its nineteenth century sequences. No material interests must be allowed to check this stupendous expansion of our knowledge.

OBITUARY NOTICES.

ARTHUR JOSEPH BREARLEY.

BORN APRIL 1, 1890; KILLED IN ACTION JUNE 20TH, 1917.

CAPTAIN A. J. BREARLEY, of the Devonshire Regiment, attached Special Brigade Royal Engineers, was reported killed in action on June 20th, 1917. Captain Brearley was a native of Birmingham, being the elder son of Mr. and Mrs. Brearley, of Small Heath, Birmingham. He was educated at King Edward's School, Camp Hill, and the High School, Birmingham, where he obtained several scholarships. He proceeded to Cambridge in 1909, where he was a scholar of Emmanuel College. In 1912 he graduated, having obtained a First Class in Part I. of the Natural Science Tripos and a Second Class in Part II. of the same Tripos. During his university career he rowed and obtained his second May colours.

Prior to the war he was science master at Exeter School. He was granted a commission in April, 1914, being promoted lieutenant in February, 1915, and captain in June of that year. He was transferred to the Royal Engineers in July, 1916, and proceeded to the front in April last year.

His brother, Sec.-Lieut. Norman Blackburn Brearley, Royal Warwickshire Regiment, was killed in action in Mesopotamia in April last year. The only surviving child, Lieut. Selwyn Blackburn Brearley, is serving with the Devonshire Regiment. Captain Brearley was twenty-seven years of age.

BERTRAM HAWARD BUTTLE.

BORN MARCH 20TH, 1888; DIED OCTOBER 1ST, 1917.

BY the death from wounds of Bertram Haward Buttle, the Chemical Society has lost one of its younger workers from whom

much might have been expected in the future, whilst those who knew him personally have lost a dear friend for whom they had the greatest respect as well as affection.

Buttle, when first I knew him, was a boy in the former People's Palace Technical Schools. After a short interval at West Ham Polytechnic, he returned to East London College and took the Science Course, graduating with Honours in Chemistry at the B.Sc. examination in 1907. After taking his degree, he went on with post-graduate work, the results appearing in the *Transactions*.*

He took up teaching, and was Science Master at Archbishop Holgate's School, York, when Professor Meldola asked me if I could recommend anyone for a demonstratorship at Finsbury Technical College. Knowing that they both possessed a common characteristic, absolute scientific truthfulness, Buttle seemed the right man, and, as might have been expected, fully justified the choice.

Almost immediately after the outbreak of war, Buttle joined the University and Public Schools Section of the Royal Fusiliers, but was drafted for service in France with the Gas Section of the Royal Engineers in July, 1915. After service with the Mediterranean Expeditionary Force in the winter of 1915—16, he returned to England, obtained his commission in May, 1916, and was in France and Belgium until last autumn, when he was wounded by an aeroplane bomb and died in hospital an hour later.

The letters of sympathy received by his parents give an idea of the impression Buttle gave of his character to those who knew him. The Rev. W. Johnson, formerly headmaster of Archbishop Holgate's School, wrote: "He was such a real man, so thorough and sincere that he gained everybody's affection in my school, both staff and boys. It is rare to find such wisdom with goodness in so young a man, and much as I felt it his advantage to leave me, I mourned his departure from my staff as that of a dear friend.

"His sense of duty was very high and his influence on my boys most excellent."

Major Monier-Williams wrote: "His death is a great grief to me, personally, as I was very much attached to him. He had been with me for several weeks and had always shown the greatest keenness and interest in his work. He was extraordinarily cheerful and willing, and nothing ever seemed to be too much trouble for him. I could always be certain that whatever I gave him to do would be well and thoroughly done."

Captain Bansell referred to the time Buttle served in his com-

* "Solubility of silver chloride in mercuric nitrate solution," 1908, **93**, 1405.

"Constitution of polynitrophenols in alkaline solutions," 1909, **95**, 1775.

pany, "where his courage and never-failing good spirits won him the love and esteem of all officers and men with whom he came in contact."

Such was Buttle, honest, industrious, keen on his work, and always cheerful and ready to do a kind action. Personally, I recall the many pleasant days spent working together. His friends mourn his loss deeply. J. T. HEWITT.

NORMAN PHILLIPS CAMPBELL.

BORN APRIL 25TH, 1886; KILLED IN ACTION MAY 3RD, 1917.

NORMAN PHILLIPS CAMPBELL was the son of Mr. James Campbell, of Montreal, and was born in Chicago on April 25th, 1886. He received his early education at the High School, Montreal, at Cliftonville, Canada, and Dulwich College.

He entered Balliol College, Oxford, in 1904, taking his degree in 1907 and becoming M.A. in 1913. Specialising in physical chemistry, he published in collaboration with Hartley papers in this journal on the solubility of iodine in water (T., 1908, **93**, 741), and a new apparatus for preparing conductivity water (*ibid.*, 428). In 1908 he decided to go to Ceylon to take up a post under the Church Missionary Society at Trinity College, Kandy, one of the largest secondary schools in the colony. On the outward voyage he carried out an investigation of the salinity of the Indian Ocean with the aid of Manley's differential densimeter, the results being subsequently published in the *Proceedings of the Royal Society of Edinburgh* (**33**, 124).

Campbell worked in Kandy from October, 1908, until the end of 1914. Although his teaching and duties as a social worker amongst his pupils (which entered very largely into his life) left him little time for research work, he carried out an investigation on the rate of crystal growth, which was published in the *Transactions* for 1915 (T., 1915, **107**, 475).

In December, 1914, he returned to England and enlisted as a private in the London Scottish, shortly afterwards obtaining a commission in the Oxfordshire and Buckinghamshire Light Infantry, and transferring to the Royal Engineers Special Brigade when it was formed. He was wounded at Loos in 1915, but was soon able to return to duty. In May, 1916, he was promoted Temporary Captain; he was killed in action on May 3rd, 1917, leaving his wife and two young children. His many friends have

cause to lament the death of a man of conspicuous ability and of singular nobility of character, whose death for his country was typical of his life of devotion to others and to his duty.

A. F. J.

EDWARD WILLIAM LANCHESTER FOXELL.

Born July 7th, 1884; Died June 11th, 1917.

Edward William Lanchester Foxell was the third son of the Rev. W. J. Foxell, Rector of St. Swithin's, E.C. He graduated in science at University College, London, under Sir William Ramsay, and was appointed in 1907 a Master in the Science School and Junior House Master in Christ's Hospital. For many years he was an officer in the O.T.C., becoming O.C. on Colonel Boardman's departure for active service. In Christmas, 1914, he resigned the O.T.C. and was gazetted Captain in the Buffs. During service at the front he fell ill with trench-fever, and died in France of appendicitis on June 11th, 1917.

Those who were so fortunate as to know Mr. Foxell intimately recognised in him a man of versatile attainments. He had a profound appreciation of all that is beautiful, whether in art, literature, or music.

MAURICE KEMP-WELCH.

Born 1880; Killed in Action April 11th, 1917.

Maurice Kemp-Welch was born at Bristol in 1880. He was educated at Clifton College and King's College, Cambridge, taking the Natural Science Tripos in 1903. He was an honorary scholar of his College.

On leaving Cambridge, he entered business life, dealing with the commercial chemistry of oils, in which he was greatly interested. He conducted a number of important experiments on wood-oil.

Immediately after the outbreak of war he applied himself to adapting German methods in rubber, and with Mr. Hadfield devised a process of coating canvas with rubber which promised well for the future. Although his concern with these devices was in the first instance commercial, the one characteristic he always showed was science for science' sake. He was on the eve of perfect-

ing some interesting researches in oils when he obeyed his country's call.

He enlisted in November, 1915, in the O.T.C. at Lincoln's Inn. He went to France with the 10th Batt. Yorkshire Regiment in June, 1916, and fought through the battles of the Somme. He was killed on April 11th near Henin-sur-Cojeuil.

Those who knew of his scientific work regret that his ingenuity, which had just begun to produce valuable results, should now be permanently lost.

He married in 1911, and leaves a widow and one daughter.

HERBERT KING.

BORN APRIL 7TH, 1876; KILLED IN ACTION OCTOBER 6TH, 1917.

HERBERT KING was born in Scarborough in 1876, in which town he received his early education, winning a scholarship to St. Martin's Grammar School, and three years later a County Major Scholarship to the Yorkshire College, the present Leeds University. After a course of three years at the Yorkshire College, he graduated in 1895 as B.Sc. with Honours in Chemistry, and also won the Senior Ackroyd Scholarship, which, however, he resigned in order to take up a teaching post at St. Martin's Grammar School, Scarborough.

He was elected a Fellow of the Chemical Society in 1897. In 1895 he became an Associate of the Institute of Chemistry, and in 1900 was elected to the Fellowship with a special diploma in pharmacology, toxicology, and microscopy. In 1901 he became a M.Sc. (Victoria), and in 1905 a M.Sc. of Leeds University.

He was a member of the Priestley Club and also of the Standing Committee of Convocation of the University of Leeds, the chairmanship of which he resigned on joining his Majesty's Forces in February, 1917.

Between 1897 and 1908 Mr. King held posts as Science Master at Dronfield Grammar School, Sheffield, Ashville College, Harrogate, Wolverhampton Grammar School, and Scarborough Municipal Secondary School. In 1908 he was appointed Head of the Chemical Department of the Cockburn High School and Technical School, Leeds, which post he held to the time of his entering the Army.

From 1909 to the time of his death he was the Public Analyst for Scarborough.

In February, 1917, Mr. King was gazetted to a commission in

the Army Ordnance Department, and after undergoing training in a special course at Woolwich, he was engaged on Government work at Portsmouth, from whence he proceeded to France in August, 1917, and was killed by an enemy bomb on October 6th of the same year.

A. J. C.

LEONARD ISON PITT.

BORN 1888; KILLED IN ACTION JULY 30TH, 1915.

A PROMISING life was cut short by the death in action of Leonard Ison Pitt. Pitt received his early education at the Coopers' Company's School, matriculated at an early age, entered East London College in 1904, and took the Final B.Sc. (London) examination in 1908 with First Class Honours in Chemistry, a month or two after his twentieth birthday.

The next year was spent at research work, which was interrupted when Pitt went to Stamford Grammar School as Science Master in 1909; at the time of the outbreak of war he was assistant head at the school. During this period, he took a great interest in agriculture and agricultural chemistry, and passed the first part of the Diploma of Agriculture at Cambridge.

After reading the above record, one might imagine that Pitt's twenty-six years of life up to 1914 had been spent entirely at work. As a matter of fact, he was a very keen sportsman, and especially excelled at football, whilst he took a considerable part in the social life of his college, endearing himself to all who knew him. Pitt was very much alive, and with his witty sayings and pleasing personality kept his immediate neighbours lively as well, whether on the football field or in the research laboratory.

He enlisted at the outbreak of war in the 8th Battalion of the Rifle Brigade, and was very proud of being one of the First Hundred Thousand of Kitchener's Army. By dint of hard work and his power of commanding men, he obtained rapid promotion and became platoon sergeant of "D" Company before many months had elapsed. He embarked for France in May, 1915, and met his death at Hooge while leading his platoon in a counter-attack on July 30th, 1915. The Officer Commanding his platoon writes:

"A better Sergeant or friend no man could wish—he met his death as only an English gentleman can—leading an attack against great odds."

A man of Pitt's great ability and many attainments naturally

had a large circle of friends, who, whilst lamenting his death, love and respect his memory. J. T. HEWITT.

ARTHUR EDWIN TATE.

DIED APRIL 22ND, 1918.

ARTHUR EDWIN TATE in 1898 entered the Durham College of Science, now Armstrong College, in the University of Durham, Newcastle-upon-Tyne, as a student in the Education Department. He graduated as Bachelor of Science in 1901, with chemistry as a principal subject. His interest in chemistry was real and living, and led him to devote his spare time to further work in this subject. While teaching in the neighbourhood of Newcastle, he worked in the College laboratories in the evenings and Saturdays, and after his appointment to the science mastership at Pontefract Grammar School he continued the experimental investigations thus begun. In 1909 he submitted the results of this work for the M.Sc., and was awarded the degree. In 1910 he was appointed senior science master of the City of Norwich School, a position which he filled with marked success. He joined the Royal Engineers in July, 1916, and went to France in the following September, where he was wounded on April 12th, 1917, and died from the effects of his wounds ten days later. Arthur E. Tate was a man of sterling qualities, a good and successful teacher. He leaves a widow, to whom he was married shortly before he joined the Army.

P. P. B.

CLAYTON BEADLE.

BORN 1868; DIED AUGUST 16TH, 1917.

CLAYTON BEADLE died at his residence at Sidcup on August 16th, 1917, at the age of forty-nine.

Mr. Beadle had been seriously ill for some time, but recovered sufficiently to undertake a long foreign tour, partly on business and partly for recuperation. Although for a time able to resume his professional duties, he was unfortunately, after a brave struggle, again laid low, and ultimately succumbed.

Clayton Beadle commenced his chemical career at the works of his cousin, Mr. Edmund Joynson, the well-known paper maker,

where he studied under Messrs. Cross and Bevan, and formed with them a lifelong friendship. After some time he became a partner in that firm, and during that period he was associated with the various industrial developments of cellulose xanthate or viscose, the name by which it is industrially known.

On the termination of the partnership, Mr. Beadle associated himself with Dr. Stevens, and with him practised as an analytical and consulting chemist. He was not only an expert in the science of paper-making, but was an acknowledged authority on matters connected with the chemistry of rubber, with which branch of industry he was intimately connected.

He also did good work in conserving the water supply of the Kent district. In this connexion, it is interesting to note that his father, Mr. Charles Beadle, gave valuable assistance to the Commission appointed to consider the condition of the lower reaches of the Thames.

Mr. Beadle made numerous contributions to technical literature, and his work was recognised by various societies, including the Royal Society of Arts, La Société d'Encouragement pour l'Industrie National (Paris), and the Franklin Institute (Philadelphia).

ALEXANDER MACOMB CHANCE.

BORN JUNE 28TH, 1844; DIED NOVEMBER 22ND, 1917.

ALEXANDER MACOMB CHANCE, J.P., was the ninth and youngest child of George Chance, of Birmingham, brother of the founders of the well-known firm of Chance Brothers & Co., of Spon Lane and Oldbury. His mother was Cornelia Maria, daughter of Arent Schuyler De Peyster, of New York, in which city George Chance lived for many years as partner with his brother William in trade with the United States.

Alexander Chance was born on June 28th, 1844, after his father's return to England. Having completed his education at Lausanne, he found employment with his relatives at their glass works at Spon Lane. The capacity that he showed soon gained for him, in 1868, the managing direction of their alkali works at Oldbury. In 1879 he was admitted a partner in the firm, and he retained the principal direction of the works, from 1901 as Chairman of the new firm of Chance & Hunt, Limited, until his retirement in June, 1912.

From the start he showed of what metal he was made. Much

wanted doing, and he did it, speedily restoring prosperity to the works and enhancing it as years went on. He was not a man of science; as he himself wrote at the beginning: "I frankly admit that my predisposition is decidedly in favour of commercial negotiations, etc., rather than of the technicalities of manufacture." He was an organiser, a director of industry, able to get the best out of his skilled subordinates by animating them with his own energy and zeal. As has been said of a modern French general, "he radiated vitality." He was ever watchful of all improvements, of new processes, of all means by which production might be increased or losses saved. Of his many successes need only be noticed here his great triumph, the Chance Sulphur Recovery Process. If he did not himself work out the chemistry of this, he directed the experiments and faced the expenditure, and in that sense may be said to have been truly the inventor of it.

Prominent among his characteristics were a singular power of quick and correct decision and a discerning knowledge of men. Those whom he gathered round him in the office, in the laboratory, and in the works formed a staff difficult to match. He treated them as friends rather than as servants, and similarly with the workmen it would be hard to find a master enjoying to a greater degree their goodwill and affection.

In social work for their benefit he was indefatigable. Institutions established at Oldbury before his time, schools, dispensary fund, mission, and relief work, he sedulously fostered, and much else he initiated or promoted, amongst them being religious endeavours, mutual help, sanitary housing, and temperance. The drunkenness that had been rampant at the works he abolished, himself taking the pledge, to the detriment of his health, to set an example. An early achievement was the Convalescent Home at Quinton, a few miles from the works, supported and managed by the men themselves, and regarded by them as their own. Other benefits to them were the Temperance Club and Institute at Langley, and the Provident Accident Fund, which he devised on the passing of the Employers' Liability Act. That Act, he saw, would cover but very few accidents, would involve long delays in its operation, and would be a fertile source of friction between masters and men. Under his scheme, the firm contributed equally with the men to a fund from which the compensation adjudged for each case was paid without question of whose fault, and instantly. One result, not perhaps foreseen, was an extraordinary diminution in the number of accidents. Undoubtedly a sense of personal interest made the men more careful.

These philanthropic activities were by no means limited to Oldbury. Alexander Chance associated himself actively with almost every movement for social advance in Birmingham and its neighbourhood. The cause of temperance found in him an unwearied protagonist. Generous to a fault himself, and giving for the love of it, he had a singular ability of persuading others to give also, and largely. If any fund of importance were to be raised, it became habitual to enlist him early in the cause. It may be questioned whether the money for the Birmingham bishopric could have been raised without his persuasive pressure on rich men. The Birmingham Young Men's Christian Association owes its great modern development and success largely to his efforts. His "St. Andrew's Guild," a work for which he received the thanks in writing of four bishops, transformed one of the worst slum parishes of Birmingham into a model of church organisation and life. His last achievement, pursued to a successful end through years of discouragement, was the acquisition of Warley Park for the use and enjoyment of the public.

His married life was of uniform felicity. His first wife was Florence, daughter of Major Arthur H. H. Mercer, 60th Rifles; his second, Agnes Elizabeth, daughter of William Fleming, of Inverness. Both entered zealously into all his social and philanthropic work. By the former, who died in 1903, he had eight children, of whom four sons and a daughter survive him. His last years he spent in quiet retirement at Torquay, where he died, worn out with work, on November 22nd, 1917.

JOHN JOSEPH EASTICK.

Born February 6th, 1855; Died September 7th, 1917.

John Joseph Eastick was born at Great Yarmouth, and in early life had his attention directed to industrial chemistry, his father being manager of the Southtown Gas Works there, and afterwards at Peel, Isle of Man. Before coming to Lancashire and taking up the systematic study of science, he had assimilated the contents of Clegg's "Gas Manufacture," and often took the keenest delight in giving his interested fellow-students an outline of the various operations in the manufacture. The early impressions thus gained lasted through life, and led him to seek the utilisation of chemical results rather than to engage in theoretical research. He gained an exhibition at Owens College and afterwards a Royal Exhibition

at the Royal School of Mines, where he secured the Associateship in Metallurgy.

Instead of following this line, he became first chemist at the sugar refinery of Messrs. Abram Lyle and Sons. From 1890 to 1894 he was manager of the Australasian Sugar Refinery, Melbourne, and acted as honorary adviser to the Victorian Government on beet cultivation and sugar manufacture. Leaving for Queensland, he spent a year on improvements of Messrs. Cran and Tooth's juice mills. During the next ten years, at Millaquin and Yengarie, he was general manager for the Queensland National Bank of their refineries, raw sugar mills, and juice mills and plantations. He was also director and chairman of the Bundaberg distillery for several years and justice of the peace for the territory. In 1906 he inspected tropical and sub-tropical agriculture in the East, but owing to failing health he returned to England.

On the death of Mr. B. E. R. Newlands, his father-in-law, Eastick took over the analytical and consulting practice of Newlands Bros. at No. 2, St. Dunstan's Hill, E.C. He took out a number of patents relating to sugar, and contributed important sections on the theory of filtration and on filtration in sugar factories and refineries to the English edition of Buehler's "Filters and Filter Presses."

Eastick leaves a widow, four daughters, and three sons, the latter of whom are carrying on the traditions of their father in applied chemistry. Tribute will always be paid to his memory by his many pupils, co-workers, and employees, and by all who were acquainted with him for his never-failing kindly advice and aid.

L. J. de Whalley.

ERNEST GEORGE HILL.

Born February, 1872; Died June 28th, 1917.

Professor Ernest George Hill, who died on June 28th, 1917, at the Ramsay Hospital, Naini Tal, from an abscess on the liver, was born in February, 1872, and was educated at Oxford, obtaining the B.A. and B.Sc. degrees of that University.

In 1895 he was appointed to the Indian Educational Service, and took up his duties as Professor of Natural Science at the Muir College, Allahabad, on December 26th of that year. He remained on the staff of the Muir College for the rest of his life. In 1911

he acted as Principal of the College, and was permanently appointed to that post in 1913.

He was for many years a Fellow of the Allahabad University, and was elected Dean of the Faculty of Science.

The Muir College of Allahabad is the most important Government College in the United Provinces, and takes the first place among the Colleges affiliated to the Allahabad University, which controls the college education of the province. The Muir College has always been regarded as a model. The buildings are fine and splendidly situated in beautiful grounds, and teaching work there is not handicapped by the very large classes which make college work so difficult in Calcutta. In these circumstances, and with this environment, Hill took a keen interest in his teaching work and remained throughout his career essentially an educationist.

In order to help his students, he prepared and published tables for qualitative chemical analysis and a handbook of practical chemistry, and his research work in chemistry was undertaken primarily with the object of making the teaching of his subject more real and interesting to his students. About that time Government officials were producing monographs on Indian industries, and Hill's attention was directed to them, with the result that he undertook a number of researches into the constitution of Indian products, and used these to stimulate the interests of his students. As in many other branches of study in India then, the courses of schools and colleges were still too rigidly modelled on European syllabuses, and were apt to be followed by the students as exotic and unpractical studies, necessary for a degree, but of no other value.

Like all those who become seriously interested in University work in India, Hill felt the importance of improving the teaching in schools in order to secure a better foundation for college education, and together with Mrs. Hill he prepared a scientific reader for use in schools.

As Principal of the Muir College and Dean of the Faculty of Science of the University of Allahabad, he was able to exert a very considerable and beneficial influence on education in the province. He was a good disciplinarian, commanding respect from his pupils, whilst at the same time he was on excellent terms with them and with his staff. He was a good cricketer and a keen sportsman; these are very valuable qualifications for anyone responsible for college education in India.

In 1910 and 1911 he rendered valuable services in connexion with the educational section of the Allahabad Exhibition.

Hill's original work in chemistry was directed partly to a study

of Indian products and partly to purely scientific problems of physical chemistry. His interest in the latter is probably to be traced to Oxford, where he returned to work during one of his furloughs. The research work started at this time secured for him the Sc.D. degree of Dublin University. A paper on "The Hydrolysis of Ammonium Salts by Water" (T., 1906, **89**, 1273), and another jointly with Dr. A. P. Sirkar on "The Electrical Conductivity and Density of Solutions of Hydrogen Fluoride" (*Proc. Roy. Soc.*, 1909, [*A*], **83**, 130), indicate the trend of his work in this field.

The first Indian product to attract his attention was the salty and alkaline earth which extends over considerable tracts in Northern India. In 1903 he published a note (P., 1903, **19**, 58) on the analysis of the salts contained in this soil. Afterwards he turned his attention to organic products, and published papers on "The coloured constituents of *Butea frondosa*" (P., 1903, **19**, 133), "A new colouring matter from *Nyctanthes Arbor-tristis*" (T., 1907, **91**, 1501), and "The root bark of *Calotropis gigantea*" (T., 1915, **107**, 1437)—the last two papers being written conjointly with Dr. A. P. Sirkar. The colouring matter from *Nyctanthes Arbor-tristis* was obtained in crystalline condition, assigned the formula $C_{20}H_{26}O_3{\cdot}OH$, and named *nyctanthin*. It was subsequently found by A. G. Perkin in *Cedrela toona* (T., 1912, **101**, 1538). From the milky latex which exudes from the broken roots of *Calatropis gigantea*, Hill and Sirkar succeeded in isolating two crystalline substances, melting at 140° and 210° respectively. These were shown to be the *iso*valerates of two alcoholic substances, *mudarol*, $C_{30}H_{47}O{\cdot}OH$, and *akundarol*, $C_{38}H_{61}O{\cdot}OH$. These alcohols were shown to give colour reactions very similar to those of cholesterol and phytosterol; on oxidation, they gave mudaric and akundaric acids respectively. In addition to these, the latex was also found to contain an oily substance, a hard, resinous substance, and a trace of alkaloid.

In addition to his work as chemist and educationist, Hill was for some time Meteorological Reporter to the Government. He also took a considerable part in the general life of the City of Allahabad. He was an enthusiastic cricketer and rider in paper-chases, and was very popular with the other Europeans in the station. For some time he was a member of the Municipal Board, where his presence was welcomed by the educated Indians, who appreciated his business capacities.

E. R. WATSON.

GEORGE THOMAS HOLLOWAY.

BORN OCTOBER 19TH, 1863; DIED OCTOBER 24TH, 1917.

GEORGE THOMAS HOLLOWAY, who died on October 24th, 1917, was born at Battersea on October 19th, 1863, and after being educated privately, entered the Royal College of Science and School of Mines, London, in 1881. Here he devoted special attention to chemistry, and obtained the Associateship of the Royal College of Science in 1884. He then served for two years as assistant demonstrator, originally under Sir Edward Frankland, and later under Sir T. E. Thorpe. He was elected a Fellow of the Chemical Society on March 4th, 1886. He afterwards proceeded to Newfoundland, and studied the resources of that colony, and also of the east of Canada. Returning to London, he commenced practice in Chancery Lane, in 1888, as analyst, assayer, and consulting metallurgist. The following year he opened testing works at Limehouse for the examination of ores on a commercial scale. In 1910 his offices and laboratories were removed to 13 Emmett Street, Limehouse. He specialised in the treatment of tin ores and the rarer metals associated therewith. He was consulted by Government departments and many mining companies. Among other work, reference may be made to inquiries, conducted for the Transvaal Chamber of Mines, in connexion with osmiridium occurring in banket ore, and the development of a zinc smelting industry in South Africa. In 1915 he was appointed Chairman of the Royal Ontario Nickel Commission, and to this work the remainder of his life was chiefly devoted. Despite an enfeebled frame and the dangers from submarines, he twice visited Canada in connexion with this inquiry; he also visited Scandinavia, and interviewed, or corresponded with, all the chief makers and users of nickel in the United Kingdom. The report, which was issued shortly before Mr. Holloway's death, occupies more than 800 pages, and is the most complete and trustworthy document which has appeared in reference to the supplies, extraction, and uses of nickel. As a result of this report, a large nickel refining plant has been established on Lake Erie, at Port Colborne in Ontario. This refinery will deal with Sudbury and other nickel–copper mattes which were formerly refined at New Jersey., U.S.A. Mr. Holloway was for years a frequent attendant at the meetings of the Chemical Society, and was interested in the Institute of Chemistry, for which body he acted as examiner in metallurgy. He was an enthusiastic supporter of the Institute of Metals; but perhaps his fullest sympathy was with the Institution of Mining and Metallurgy, on the council

of which he served for many years, and filled the office of vice-president. He was a member of the London section of the Society of Chemical Industry, and a not unfrequent contributor to the journal of that society. Among other appointments, he had served as examiner in metallurgy in the University of Birmingham, assistant examiner to the Board of Education, and juror in the Franco-British Exhibition of 1900. His clearness of intellect, kindliness of manner, unassuming character, and perfect honesty of disposition endeared him to a wide circle of friends, not only in this country, but throughout the British Empire. He was an honorary member of the Chemical, Metallurgical, and Mining Society of South Africa, and acted as corresponding member for the United Kingdom. With a few words taken from the Journal of the South African Society this short notice may suitably close: "It may be fittingly said of him that men of his high character and conduct do much to raise the status of the profession of which he was so distinguished a representative." T. T.

EDMUND ALBERT LETTS.

BORN AUGUST 27TH, 1852; DIED FEBRUARY 19TH, 1918.

EDMUND ALBERT LETTS was born at Sydenham, Kent. His father, in addition to Clare Lodge in Sydenham, owned South View in the Isle of Wight, and there Letts appears to have spent the happiest part of his boyhood, for in later years he often spoke of the place with affection.

His education began at Bishop Stortford School, and was continued at King's College, London, after which he studied at the Universities of Vienna and Berlin.

In 1872 he became chief assistant to Crum Brown in the Chemical Department of Edinburgh University. Four years later, at the early age of twenty-four, he was appointed first professor of chemistry in University College, Bristol, a post in which he was followed by Ramsay. In 1879 he was elected to succeed Andrews in the chair of chemistry in Queen's College, Belfast, and this position (subsequently changed to a professorship in the Queen's University of Belfast) he held until 1917. After his retirement, he spent part of his time in the south of England, and in January, 1918, he left Belfast on a visit to Ventnor. He was a keen cyclist, and took his bicycle with him, spending his time riding about the neighbourhood in which he was staying. On the evening of

February 18th he was out by moonlight, and, while coming down Zig-zag Road about 7.30 p.m., he lost control of his machine and crashed into a wall. He never fully recovered consciousness, and died the following morning about 10 a.m.

His scientific work falls into three main divisions. Up to 1890, his main interest lay among the organic compounds of phosphorus and sulphur, and his investigations in this field gained him the Keith Prize, which was awarded to him in the period 1887—1889 by the Royal Society of Edinburgh. Thereafter he carried out researches on atmospheric carbon dioxide until 1902. His final work was concentrated on the sewage problem, and the results are to be found in Appendix VI. of the 5th Report of the Royal Commission on Sewage Disposal, and also in Appendix III. to the 7th Report of the same body, the work being done in conjunction with Dr. Adeney and Mr. E. H. Richards.

To speak of Letts's personal side is a difficult task for one who only knew him towards the end of his life; but one characteristic stands out above all others—his unfailing kindness to a new and younger colleague. He had complete trust in his staff and showed an unfeigned pleasure in the research output of the laboratory, whether it was his own or was carried out by others, for he had not a spark of that jealousy which at times induces a senior to appropriate the work of a junior colleague. In the distribution of research students among the members of the staff he was more than generous, and his colleagues never had to fear that a student trained by them would be appropriated by Letts as soon as merit was shown. This was not due to indifference, for in his own research room he carried on a steady stream of investigations.

In his personal characteristics, Letts was one of that rare species, "a fine old English gentleman." His reserve, his innate dignity, his impressive presence, and his command of polished oratory all stood him in good stead in the lecture theatre of a university where the students are noted for their high spirits; and the same qualities were valuable to him in other academic relations, for he was one of the leading figures on the staff.

As a chemist, he had a tenacity of purpose so strong that once he had begun an investigation he would never leave it until he was sure that he had carried it as far as he could. "So-and-so used to tell me to drop it," he sometimes said, "but I always find that something comes out if one holds on long enough." He was a neat manipulator and an expert glass-blower.

His outlook on chemistry was a wide one, and his interests tended towards what he called "the philosophy of chemistry." His book, "Some Fundamental Problems of Chemistry, Old and New,"

showed that he was alive to the most recent developments of the subject, and, by its originality in the choice of subjects, it stands apart from the ordinary run of text-books.

He was a Fellow of the Royal Society of Edinburgh and of the Institute of Chemistry. In 1881, the Royal University of Ireland conferred on him, *honoris causa*, the degree of D.Sc., and in 1909, when the Queen's University of Belfast was founded, he was one of the first members of Senate appointed. A. W. S.

PETER MacEWAN.

BORN MAY 29TH, 1856; DIED MAY 16TH, 1917.

PETER MACEWAN, of Highgate, London, who was elected a Fellow of the Chemical Society in 1886, was born at Lochee, Forfarshire, on May 29th, 1856. He was educated locally, and was apprenticed to pharmacy with Mr. John Peebles (now Judge Peebles, of Kirkcaldy), and afterwards became an assistant in his uncle's business at Dundee. His instruction in chemistry was obtained under Mr. Frank Young at the Dundee Science Schools, now the Technical College. He passed the qualifying examination of the Pharmaceutical Society in 1878 and became a pharmaceutical chemist in 1880, acting for a short time as a pharmaceutical tutor. An analytical chart for chemistry students which he devised received a wide recognition for utility. In 1882 he was appointed Secretary in Scotland of the Pharmaceutical Society, took charge of the North British branch in Edinburgh, and made all arrangements for the removal to the present premises. A good deal of his time was spent in chemical research work during his tenure of office, one of the first pieces of work being on the iodo-allyl compounds. He was led to take this up by receiving a sample of liniment of iodine which had caused severe blistering when applied to the skin. An investigation showed that the liniment had been compounded with methylated spirit, and he found that allyl alcohol present in the wood spirit used for denaturing purposes had formed an iodo-allyl compound of a particularly irritating nature. Referring to this research, he was fond of recalling how, his eyes streaming with tears, he received visitors to the Pharmaceutical Society's Museum, and it was sometimes assumed that he was suffering from great grief instead of from his devotion to science. The unstable character of sweet spirit of nitre and the changes that take place on keeping attracted his attention. He found that the diuretic

properties of this old galenical were not due entirely to ethyl nitrite, because old specimens from which ethyl nitrite had disappeared still retained considerable medicinal activity. He simplified the process of estimating the strength of the spirit, and when the late A. H. Allen, of Sheffield, devised the nitrometer, it became possible for the pharmacist to estimate the strength of sweet spirit of nitre within five minutes. Mr. MacEwan also directed attention to the large proportion of sodium carbonate, from 20 to 35 per cent., present in some samples of sodium nitrite, and showed that there should be no difficulty in obtaining a product containing 98 per cent. of sodium nitrite if lead or copper were employed as deoxidising agents for the nitrate. Several of his papers dealt with essential oils, particularly camphor oil and eucalyptus oil, these being at that time recent introductions into medicine. In after years, Mr. MacEwan often regretted that his work on camphor oil was not completed, but he had succeeded by distillation in separating out several of the constituents of this complex substance. The chemistry of Calabar bean and the preparation of solution of bismuth ammonio-citrate were other investigations which he undertook, and he substantially enhanced the interest and value of the scientific meetings of the North British branch of the Pharmaceutical Society. The allocation of a portion of the Hanbury collection of Chinese drugs to the museum caused Mr. MacEwan to take up the study of Chinese, and he obtained sufficient acquaintance with that difficult language to enable him to make translations of the labels and classify the drugs intelligently. In 1885 he was appointed assistant editor of *The Chemist and Druggist*, having attracted the attention of the editor by a clever and laborious codification of the chief pharmacopœias of the world, which he carried out with the object of forming a basis for an international pharmacopœia. On the retirement of Mr. A. C. Wootton in 1899, he succeeded to the editorship, and from that time specialised in the various legal enactments dealing with the drug trade, for example, the Medicine Stamp Acts, the poisons laws, the Sale of Food and Drugs Acts, and the spirit laws, while keeping always in close touch with the latest developments in chemical and pharmaceutical science. He contributed a number of papers on ethical subjects to various pharmaceutical bodies. He visited America in 1893, and made many friends among American men of science. In 1909 he went to Germany for the International Congress of Pharmacy, where, in collaboration with Mr. G. P. Forrester, F.C.S. (who has been interned in Germany since the outbreak of war), he contributed a paper on the standardisation of potent medicinal preparations. He

was a member of the Society of Chemical Industry, a corresponding member of the Société de Pharmacie, Paris, Secretary of the Commission on Variation in Activity of Potent Drugs (set up by the International Congress of Applied Chemistry in 1909), and connected with most of the drug trade organisations of this country. Mr. MacEwan was the author of "The Art of Dispensing," which is the standard work in the English language on the dispensing of medicines, and of "Pharmaceutical Formulas," a receipt book for chemists and druggists, of which works many thousand copies have been sold. Of his personal character much could be written, but the outstanding features were his kindness, geniality, "pawky" humour, and indefatigable industry. The strong love of his native country which he had was shown by his yearly visits to the Highlands and his connexion with such bodies as the Scottish Corporation, the Caledonian Society, and the London Forfarshire Association. His end came with great suddenness from an attack of apoplexy, although during the previous winter he had had a severe illness, which acted as a warning. Thus he "laid down the well-worn tools without a sigh" in the plenitude of his powers and with his faculties unimpaired, bequeathing to his friends a lofty ideal and an inspiring example. S. W. W.

LUDWIG MOND.

BORN MARCH 7TH, 1839; DIED DECEMBER 11TH, 1909.

LUDWIG MOND was born at Cassel on March 7th, 1839. His father, Moritz B. Mond, was a merchant of that city. His mother's maiden name was Henriette Levinsohn.

Mond was educated at the Realschule and the Polytechnic School at Cassel, and then went, in 1855, to study chemistry under Hermann Kolbe at Marburg.

In the following year, 1856, he proceeded to Heidelberg, and so, having followed the great teacher through two institutions, still marked by his influence, he came under the actual control of Robert Wilhelm Bunsen. From him, during a three years' course, Mond undoubtedly acquired that absorbing love of pure chemical science that was so characteristic of him in after life.

His introduction to industrial activity took place at a small Leblanc soda works at Ringenkuhl, near Cassel. Here, the continual waste of sulphur speedily attracted his attention, and he began in 1860 those researches which ultimately led to the invention of his well-known recovery processes.

He left Ringenkuhl to become manager of a factory at Mainz for producing acetic acid by the distillation of wood, and from there went to Cologne to engage in the manufacture of ammonia from waste organic matter, especially leather.

After spending some time in one or two other factories, both in Germany and Holland, he came to England in September, 1862.

Mond's experience at Ringenkuhl led to his patenting a process for the recovery of sulphur from Leblanc alkali waste by atmospheric oxidation, lixiviation, and subsequent separation of sulphur by treatment of the liquors with hydrochloric acid. This process was patented in France in December, 1861, and in England in August, 1862.

Entering the works of John Hutchinson and Co. at Widnes in order to demonstrate the working of his process, and if possible to sell his patent, Mond speedily found that it was not entirely adapted for large-scale operations, where the cost of labour was an important consideration, and he patented an improvement on September 8th, 1863.* This consisted of carrying out the oxidation in the "black-ash" lixiviating vats by blowing air through the waste and repeating the operation after one or two washings with water. Subsequently, Mond introduced the use of waste liquor from chlorine stills in place of fresh hydrochloric acid for the decomposition of the soluble sulphur compounds, with the separation of free sulphur.

In 1864 he undertook the construction and management of a Leblanc soda works at Utrecht, and remained there for three years.

Shortly before his return to Widnes, in 1867, he married his cousin, Frida Löwenthal, daughter of Adolf Löwenthal, who was one of the pioneers of German electro-plating and electro-chemical industry. Lifelong familiarity with scientific problems eminently fitted Mrs. Mond to be the companion of such a man as her husband, and to the end of his life she never failed to take the most intense interest in all his work.

When Mond returned to England, and became a naturalised

* "On the manufacture of sulphur from alkali waste in Great Britain," by Ludwig Mond:—Read before the British Association at Norwich, 1868. *Chem. News*, October 2nd, 1868:—

"On the recovery of sulphur from alkali waste," by Ludwig Mond; Pamphlet published by W. B. Jones & Co., South Castle Street, Liverpool.

"On the probable effect of the general adoption in Great Britain of Mond's process for the Recovery of Sulphur from Alkali waste from a mercantile point of view," being a paper communicated to the River Pollution Commissioners at their request by Ludwig Mond—G. G. Walmsley, 50, Lord Street, Liverpool, 1870.

British subject, he rejoined Messrs. Hutchinson, perfected his sulphur recovery in their works, and introduced it to many others. This and the Schaffner process continued to be worked until they were displaced by the Chance process.*

In 1872 Mond made the acquaintance of Ernest Solvay, a Belgian chemist, who was interested in the process of making carbonate of soda invented by Harrison Gray Dyar and John Hemming in 1838.† Solvay, in association with his brother Alfred, had built and was running a small factory at Couillet, near to Charleroi. They were not by any means the first who had endeavoured to convert the simple reaction of Dyar and Hemming into a manufacturing process, nor was their experience of difficulties dissimilar from that of their predecessors either on the technical or the financial side; but, by the application of scientific skill, the exercise of boundless patience and tireless application to work, they were beginning to surmount one obstacle after another.

While at Messrs. Hutchinsons' works at Widnes in 1862, Mond had become the friend of Mr. (now the Rt. Hon. Sir) John Tomlinson Brunner, who was in the commercial department of that firm, and when a study of Solvay's works convinced Mond that there were chances of a brilliant future for an ammonia-soda process, he entered into partnership with Brunner and obtained a licence to work Solvay's process in England.‡

With some difficulty they obtained sufficient capital to enable them, in 1872, to purchase the Winnington Park Estate, Northwich, from Lord Stanley of Alderley, and to erect small works thereon. Whereas the Leblanc process starts with solid salt, the ammonia-soda process requires salt in solution, and so a Cheshire site was selected for the works, because saturated brine was readily obtainable in the immediate neighbourhood.

With the starting of the works in 1873 there commenced a period of trouble that lasted for six or seven years. Although the reactions $NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl$ and $2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$ take place most readily as discovered by Dyar and Hemming, the process becomes more complicated when the raw materials are impure, when all operations have to be carried out in closed vessels to avoid loss of ammonia, and when the apparatus itself is apt to be destroyed by the corrosive action of some of the reagents. The problem of convert-

* G. Lunge, "Sulphuric Acid and Alkali," 2nd edit., 2, 827–851.

† Dyar and Hemming, E.P., 7713 of 1838: Improvements in the manufacture of carbonate of soda.

‡ E.P., 3131 of 1863, E. Solvay—Apparatus by means of which the formation of carbonate of soda by direct combination is rendered practically available for manufacturing purposes.

ing an interesting chemical experiment into a lucrative commercial process had baffled all the earlier manufacturers, and although Solvay had achieved quite an appreciable measure of success, the gigantic task of evolving an economical continuous process carried on in scientifically designed apparatus was reserved for Mond.

No man was better fitted for the undertaking. Endowed with a quick and fertile brain, he readily grasped the reasons why troubles arose, and his thorough training in pure science enabled him to guard against their recurrence. A tireless worker himself, he had no patience with those whose energies were not sustained. Although his house was within one hundred yards of the works, he frequently spent his nights in the factory, taking such rest as he could secure on a bed arranged in the foreman's office in the midst of the plant. Gifted with powerful determination, he could never contemplate his own failure, and had little sympathy for such as admitted theirs.

A friend was once asking him not to be too hard on a man who had failed to achieve a successful result in a task which had been allotted to him, and urged that the man had done his best, when Mond said: "Heaven help the man who does his best and fails; there is no other hope, and I have no use for him."

By living in the midst of his work, in those early days, Mond set a wonderful example to his assistants and men. His methods of manufacture were absolutely scientific; there was no "rule of thumb" practice. Appearance, taste, and smell did not satisfy him; he took nothing for granted.

One characteristic example is perhaps worth quoting, because it is so typical of his method of teaching in a manner not easily forgotten. Three of his assistants once reported to him that a certain boiler employed for heating brine was constantly getting stopped up with sand. Mond expressed surprise, and accompanied the three to view it. He was shown the sand, and listened for a short time to the various theories propounded of how it came from the brine shaft. He suddenly turned to one and said: "Bring me some hydrochloric acid." When provided with this, he poured it over the "sand," and this promptly dissolved with free evolution of carbon dioxide. Turning to the assistants, he said: "Now where is your sand? You are a nice lot of chemists."

For seven arduous years Mond struggled with the problems which the process presented; but gradually, by successive inventions, he so transformed the methods of manufacture that by the year 1880 he was able to claim that the ammonia-soda process was a commercial success.

Brunner, Mond and Company were not without competitors in

working the Solvay process in England, for, in 1874, Messrs. Richards, Kearne, and Gascoigne had started works at Sandbach in Cheshire, under licence from Solvay. Their venture, however, was not successful, and the works were sold to Brunner, Mond and Company in 1878.

In 1881 the undertaking was converted into a limited company with £600,000 capital, and works at Winnington and Sandbach. Brunner and Mond became managing directors. To-day the nominal capital stands at £10,000,000, and the company owns six factories and has controlling or other interests in several more.

In his endeavour to produce soda more economically by the ammonia process than it could be manufactured by that of Leblanc, Mond was naturally anxious to obtain cheap ammonia. We have seen that, in 1861, he was engaged in the production of ammonia from waste material of animal origin, and he stated that he then observed that the yield by no means corresponded with the nitrogen in the raw material.

In 1879 he determined to make a complete study of the problem of how to manufacture ammonia cheaply.* With the object of testing the value of already known processes for obtaining ammonia from the nitrogen of the air, he engaged Mr. Joseph Hawliczek to carry out the experimental work. All the processes investigated gave unsatisfactory results, with the exception of one, and that was the barium cyanide process invented by Margueritte and Sourdeval. This consists in heating a mixture of barium carbonate with carbon in the presence of nitrogen, and then treating the resulting barium cyanide with steam, thus producing ammonia and regenerating the barium carbonate.

The experiments proved so promising that Mond designed apparatus for carrying out the manufacture on a fairly large scale. The formation of cyanides by this method, however, requires a temperature of from 1200° to 1400°, and Mond ultimately found that his special clay retorts would not last in this great heat, and he was compelled reluctantly to abandon the process. Among the tested processes for obtaining ammonia from the nitrogen of the air was one patented by Rickman and Thompson, who claimed that by passing air and steam through a deep coal fire the nitrogen is to a certain extent converted into ammonia. Mond found that it certainly yielded a considerable quantity of ammonia, but he discovered that, if the same coal were burned in an externally heated tube in a current of steam alone, it gave double the amount. He made large scale experiments in this direction, but came to the

* Presidential Address to the Society of Chemical Industry, 1889, by Ludwig Mond.

conclusion that, although the yield of ammonia was large, the process could never be economical. He saw, however, that if coal could be burned in gas producers by a mixture of air and steam, the plant could be simple, and the gas obtained could be utilised in the same way as ordinary producer gas.

He therefore constructed gas producers and ammonia-absorbing plant at Winnington, and experimented with different classes of fuels for a number of years. These showed that the yield of ammonia varied inversely with the temperature at which the producer was worked, and that the temperature could be controlled by regulating the amount of steam admitted with the blast; the lower the temperature, the higher was the yield of ammonia. Considering the cost of steam, he found that the best practical results were obtained by introducing about two tons of steam for every ton of fuel gasified. He succeeded in converting one-half of the nitrogen existing in the fuel into ammonia, getting about 8 kilos. of ammonia per ton gasified. The gas obtained (now known as "Mond gas") contained about 15 per cent. of carbon dioxide, 10 per cent. of carbon monoxide, 23 per cent. of hydrogen, 3 per cent. of ethylene, and 49 per cent. of nitrogen. This was used for heating furnaces and working gas engines, and proved so satisfactory that a large plant was installed at Winnington.

Having now satisfied himself that his process could yield a cheap gas suitable for almost every manufacturing operation, Mond sought to extend its use throughout the world. He formed the Power Gas Corporation to grant licences under his patents, to act as technical advisers to, and erect plants for such manufacturers as desired to employ the gas.

Mond's statement that his gas could be generally employed in manufacture met with strong criticism from iron makers, who said that, on account of its low calorific power, it could never be used for making steel.

With characteristic energy, Mond immediately built a Siemens steel furnace at Winnington and made steel there for some weeks, inviting the steel makers to come and see it.

Recognising that the gas was eminently suitable for small furnace and foundry work, and that it ensured smokeless combustion, Mond was instrumental in founding the South Stafford Mond Gas Company in the heart of the Black Country, at Tipton, near Dudley Port. Here, fuel is gasified in Mond producers, and, after purification, the gas is compressed and delivered into mains that convey it to consumers in about 160 works.

Mond stated in his Presidential Address to the Society of Chemical Industry in 1889 that if one-tenth of the 150 millions

of tons of fuel annually consumed in England were treated by his process, the production of sulphate of ammonia would be large enough to enable us to supply the whole of the Old World, and would render us independent of the New for supplies of nitrate of soda for fertilising purposes. He spoke, of course, in ignorance of the enormous consumption of nitrates which a modern war would involve, but when we, with our later knowledge, recognise the readiness with which an "Ostwald" process can convert ammonia into nitric acid, we can confidently depend upon a moderate development of his process rendering England independent of Chile.

English Mond gas producer works in operation are using bituminous coal, but the Italian installations at Lucca and Orentano are working with lignite. The process has also been applied to the gasification of peat.

In his anxiety to obtain cheap ammonia for the ammonia-soda process, Mond's attention was attracted to by-product coke ovens, and, as the soda process requires coke for its limestone burning, Brunner, Mond and Company erected the first English installation of Semet-Solvay ovens.

In 1884, Mond made London his regular place of residence in order to live in close association with scientific societies. He first resided in Park Crescent, but later acquired The Poplars, 20, Avenue Road, Regent's Park. This house formed his headquarters all the rest of his life; there he started a laboratory for his research work, and made his house a centre for scientific and artistic friends. In order to escape the rigours of the English climate, he spent most of his winters in Rome, at his house the Palazzo Zuccari.

One of the first inventions emanating from the new laboratory was a gas battery (*Proc. Roy. Soc.*, 1888, **46**, 296). Mond obtained the assistance of Dr. Carl Langer, and attempted to discover whether it was possible for a gas so rich in hydrogen as Mond gas to be as directly converted into electricity as pure hydrogen. Starting with the construction of the cell described by Lord Justice Grove in 1839, and working with pure hydrogen, they found that its operation was so tardy that they were led to seek for more suitable electrodes.

After a long series of experiments, they evolved a cell which consisted of a number of elements. The strips of platinum foil as used by Grove, partly immersed in dilute sulphuric acid, gave place to porous diaphragms of inert material, such as plaster of Paris, impregnated with acid, and these were covered on each side with very fine platinum leaf perforated with numerous small holes and covered with a thin film of platinum black. It became

practically a dry battery. A number of these elements are placed side by side with non-conducting frames between to form chambers, so that hydrogen can be passed along one side of the element while the other side is exposed to air.

Mond and Langer found that a battery consisting of seven elements, with a total effective surface of half a square metre, contained 2·5 grams of platinum leaf and 7 grams of platinum black, and gave a current of 2 amperes and 5 volts or 10 watts, equal to nearly 50 per cent. of the total energy obtainable from the hydrogen absorbed. Having so constructed an efficient battery, they next proceeded to employ producer gas in lieu of hydrogen alone. They discovered that unless the gas were deprived of its carbon monoxide and hydrocarbons prior to use, the efficiency of the platinum black rapidly disappeared. In seeking for a cheap method of removing these gases at the temperature of gases leaving the producer, they discovered that if such gases were passed with the steam which they contained over finely divided metallic nickel or cobalt, the carbon monoxide was converted into carbon dioxide and carbon, whilst the hydrocarbons yielded carbon and hydrogen.* They found that when the producer gas was thus purified and enriched in hydrogen it yielded good results with the battery; but, unfortunately, the life of the battery itself proved of short duration.

In connexion with the work on the gas battery, Mond undertook a research in company with Sir William Ramsay and Dr. John Shields on the occlusion of oxygen and hydrogen by platinum and palladium (*Proc. Roy. Soc.*, 1894, **58**; *Phil. Trans.*, 1897, **190**; 1898, **191**).

Pressure of other important work unfortunately prevented Mond from solving the problem of how to construct a battery to endow it with a long life.

By 1886 the ammonia-soda process had developed to such an extent that it had become a serious competitor of the Leblanc process; but as such it possessed one defect, inasmuch as it wasted all the chlorine of the sodium chloride, and so produced no bleaching powder.

This was recognised by Mond as early as 1882, and he patented a process for manufacturing calcium peroxide to be used as a substitute for bleaching powder. He followed this in 1883 by a process for obtaining hydrochloric acid. In the ammonia-soda reaction, the chlorine remains in solution, in combination with ammonia, along with residual sodium chloride. Mond concentrated this liquor by heat, and, after the removal of the first

* L. Mond and C. Langer, "Improvements in obtaining hydrogen," E.P., 12608 of 1888.

crystals of common salt, obtained the ammonium chloride in a solid form. This, on treatment with sulphuric acid, yielded hydrochloric acid and ammonium sulphate.

In 1886 (E.P., 66 of 1886) he invented a process for obtaining chlorine by passing the vapour of ammonium chloride over nickel or a similar active oxide to form the corresponding chloride with liberation of ammonia, subsequently treating the chloride with hot dry air to liberate chlorine and regenerate the oxide. By employing superheated steam in place of dry air, he obtained hydrochloric acid instead of chlorine (E.P., 65 of 1886). The process for the manufacture of chlorine was installed at Winnington, and bleaching powder was made by it for several years. The concentration process for obtaining ammonium chloride was superseded by a cold one, wherein the liquors were reduced in temperature by freezing machines until the ammonium salt separated. This was found to yield a product of great purity, an essential property for a salt which had to be volatilised. The dried ammonium chloride was volatilised by heat, and the vapours were passed over nickel oxide. This yielded nickel chloride and allowed free ammonia to pass forward for absorption in water and eventual return to the soda process. Chlorine was obtained by passing a current of hot dry air over the nickel chloride, and was utilised in Deacon chambers for the production of bleaching powder. In order to secure the exposure of a large surface to the action of the gases, Mond made up the nickel oxide into pills by mixing it with china clay and pressing it between rollers with hemispherical cavities. He found that when these pills had been in use for some weeks they became black, swelled up, and ultimately fell into powder. Investigation showed that, in this condition, they contained a considerable quantity of carbon. This was found to owe its origin to the constituents of the so-called "inert gas" which was employed to sweep out the last trace of ammonia from the apparatus before proceeding to evolve chlorine. This gas was obtained from the exits of the ammonia-soda precipitation towers, and consisted of nitrogen mixed with some carbon dioxide and carbon monoxide. A study of the behaviour of these gases in the presence of nickel oxide and their action on metallic nickel led Mond and Langer not only to devise the method previously mentioned of removing carbon monoxide from producer gas, but also to the discovery of nickel carbonyl.*

The plant employed for the volatilisation of ammonium chloride had to be of special construction on account of the violent attack of the vapour on most metals. The valves which were required

* "The history of my process of nickel extraction," by L. Mond, *J. Soc. Chem. Ind.*, 1895, **14**, 945.

for effecting the changes of current were made of nickel. Although laboratory experience had shown this metal to be proof against attack by ammonium chloride vapour, the valves in the manufacturing process soon became leaky, and were found to be coated with carbon. Mond and Langer were thus led to make a careful study of the action of carbon monoxide on nickel with the view of ascertaining whether a definite compound of nickel and carbon was formed. In the course of experiments, finely divided nickel was treated with pure carbon monoxide in a glass tube at varying temperatures for a number of days, and was then cooled in a current of carbon monoxide before it was removed from the tube. In order to keep the poisonous carbon monoxide out of the atmosphere of the laboratory, the gas escaping from the apparatus was connected to a Bunsen burner and lighted. To their surprise they found that, while the tube was cooling, the flame became luminous and the luminosity increased as the temperature fell below 100°. The flame gave a mirror on a cold porcelain plate, and when the glass exit tube of the apparatus was heated, a metallic mirror was obtained inside, whilst the Bunsen flame lost its luminosity. The mirror was found to consist of pure nickel. Eventually they were successful in discovering that, at a temperature below 100°, nickel combines with carbon monoxide to form a tetracarbonyl which is a colourless liquid boiling at 43° and solidifying at 25° to form needle-shaped crystals (Mond, Langer, and Quincke, T., 1890, **57**, 749; Mond and Langer, *ibid.*, 1891, **59**, 1090).

Owing to the disintegration of the nickel pills, Mond substituted magnesia and obtained satisfactory results. The chlorine process was carried on for several years; but the plant proved costly in repairs, and the heat losses were considerable. Although the raw material, ammonium chloride, was ready to hand in solution with other compounds, the separation and drying of the pure salt could not be effected cheaply, and proved a serious handicap to a process which had to compete with those that started with common salt. The process was therefore abandoned in favour of one patented by Carl Hoepfner, by which zinc oxide and calcium chloride under treatment with carbon dioxide yield zinc chloride and calcium carbonate. The zinc chloride on electrolysis gives chlorine and pure zinc. Thus the residual liquors from the ammonia-soda process were made to yield their chlorine, and the zinc was obtained in a state that commanded a high price.

In investigating the properties of nickel carbonyl, Mond was impressed with the ease with which nickel could be converted into a volatile gas by the action of carbon monoxide, and recognised that it might afford a method of separating this metal from others on a manufacturing scale. He was at first averse to undertaking

the creation of an entirely new industry himself so late in life, and proposed to sell his patent; but, as he failed to find a purchaser, he erected plant in 1892 in the Wiggin Nickel Works at Smethwick, near Birmingham, and placed it in the charge of Dr. Carl Langer. For such a novel process, all the plant had to be designed and constantly altered through the first four years of arduous work. When the practicability of the process had been fully demonstrated, Mond formed the Mond Nickel Company, and handed over to it the future developments of the manufacture. He became its first chairman, and retained the office until his death. In addition to the labour involved by the construction of large works at Clydach, near Swansea, the company had to acquire and develop mines and ore-handling plant in Ontario, Canada. Although in all this work he was ably assisted by his two sons, together with Dr. Langer and Dr. B. Mohr, the bulk of the work fell upon Mond, for, with his characteristic thoroughness, he insisted upon personally examining every detail.

He had the satisfaction of seeing his process become of immense commercial importance, and the company rewarded with phenomenal success. The Clydach Works, managed by Dr. Langer, have been repeatedly enlarged, and now produce annually upwards of 3000 tons of 99·9 per cent. nickel.

The details of the process were well described by Roberts-Austen before the Institute of Civil Engineers in 1898 (*Proc. Inst. Civil Eng.*, 1898, 135). The discovery of such an astonishing compound as nickel carbonyl led Mond to investigate the action of carbon monoxide on other metals. He soon succeeded in preparing iron carbonyl, but found that, at the ordinary pressure, no results were obtained with any of the large number of metals which he employed. At high temperature and under extreme pressure, however, he succeeded later in obtaining carbonyl of cobalt at 100 atmospheres and 200°, of molybdenum at 250 atmospheres and 200°, and of ruthenium at 450 atmospheres and 300° (*Seventh Inter. Congress App. Chem.*, 1909).

The account of this work, carried out with the assistance of Dr. Hirtz and Mr. Cowap, formed the substance of the last publication under Mond's name (T., 1910, **97**, 798).

The four strenuous years devoted to the placing of the nickel process upon a firm industrial basis undoubtedly overtaxed Mond's strength. He had suffered from a weak heart for several years. The unfortunate death of three workmen, due to inhaling some of the poisonous nickel carbonyl, deeply affected him, and the sudden death in Egypt of his daughter-in-law, Mrs. Robert Mond, completely broke him down.

He presided over the Inorganic Section of the Seventh Inter-

national Congress of Applied Chemistry held in London in the summer of 1909, and entertained the members at a garden party at The Poplars, Avenue Road. In the late autumn he suffered much from sleeplessness, and his health visibly declined. He had intended to winter in Rome, but was never sufficiently well to bear the journey. He died at his house on December 11th in his seventy-first year, and was laid to rest on the 14th in the mausoleum at Finchley, which he had built to receive the bodies of himself and his family. The funeral was most impressive. Standing on the top of the wide stone steps which lead to the upper part of the mausoleum, the Jewish Rabbi conducted the service in Hebrew. Ranged below him stood men eminent in science, art, and industry; Mond's two sons, his old partner and friend Sir John Brunner, Ernest Solvay, directors, managers, foremen, and old workmen from the factories with which he was connected, and chemical manufacturers. These, from far and near, along with a group of chemists containing those who had been associated with him in his researches, seemed to represent every phase of his life. Whatever was the sense of personal loss, each felt that science and industry had lost a great man. He was recognised by all as an ideal industrial pioneer. With all his love of pure science, he was never led to make interesting researches which had no definite object. He never undertook work which was unlikely to prove of industrial utility. His financial success was great, but this was not regarded by him as the reward which he desired for his work. He never worked for the purpose of making money, but for the sole object of cheapening manufactured products. In his fortuitous partnership he owed his financial success just as much to the commercial genius of Sir John Brunner as the latter, in turn, was indebted to the scientific ability of Mond.

No words can more fitly describe Mond's attitude of mind in connexion with his work than those used by himself in concluding his presidential address to the Society of Chemical Industry in 1889. He said:

"The statement is frequently made that 'Necessity is the mother of Invention.' If this has been the case in the past, I think it is no longer so in our days, since science has made us acquainted with the correlation of forces, teaching us what amount of energy we utilise, and how much we waste in our various methods for attaining certain objects, and indicating to us where and in what direction, and how far, improvement is possible; and since the increase in our knowledge of the properties of matter enables us to form an opinion beforehand as to the substances we have available for obtaining a desired result. We can now foresee, in most cases, in what direction progress in technology will move, and, in con-

sequence, the inventor is now frequently in advance of the wants of his time. He may even create new wants, to my mind a distinct step in the development of human culture. It can then no longer be stated that 'Necessity is the mother of Invention'; but I think it may truly be said that the *steady methodical investigation of natural phenomena is the father of industrial progress.*"

He had no great faith in the value of teaching technological or industrial chemistry in special laboratories or institutions, for he held that a man could only become a successful industrial chemist when he had received a complete training in pure science.

In his speech to the students assembled at the opening of the Schorlemmer Laboratory for Organic Chemistry, Manchester, in May, 1895, he advised them to devote their attention to the study of pure science alone without giving any thought to immediate practical results.

In order to foster scientific research, Mond purchased a house, formerly the town residence of Lord Albemarle, adjacent to the Royal Institution, and after converting it into a laboratory, fully equipped with apparatus at a cost of £45,000, presented it to the nation along with a sum of £62,000 as endowment, requesting that the building should be called the Davy-Faraday Laboratory. His idea was to provide a place where an investigator could secure the means of pursuing his researches under the best possible conditions without the expenditure of large sums of money.

All through his life Mond never failed to point out to his assistants that, in order to avoid waste of time and for the purpose of securing a favourable start, they should read all that had been published on the subject before they started any new investigation. In his later years, he recognised that in the face of the multiplication of scientific publications it became year by year more difficult to ascertain what had been written. In order therefore to facilitate the consultation of the world's publications, he presented the Royal Society with a sum of £14,000 to defray the cost of the regular compilation of a catalogue of international scientific literature.

Great as was the fortune which Mond amassed, no less princely was his liberality. What he gave privately to those on whom fortune had not smiled is known to very few. It is, however, certain that of those who solicited help from him, none but such as were proved to be unworthy failed to receive it.

Mond was the recipient of the following honours:

He was instrumental in founding the Society of Chemical Industry, and was elected its first president in 1881, and was again president in 1889.

He was elected a Fellow of the Royal Society in 1891.

Doctor of Science (*honoris causa*) of the University of Padua in 1892.

Doctor of Science (*honoris causa*) of the University of Heidelberg in 1896.

Foreign member of the Reale Accademia dei Lincei of Rome in 1899.

Doctor of Science (*honoris causa*) of the University of Manchester in 1904.

LL.D. (*honoris causa*) of the University of Oxford in 1907.

Honorary member of the German Chemical Society in 1908.

Grand Cordon of the Crown of Italy in 1908.

Honorary foreign member of the Royal Society of Naples in 1908.

Foreign member of the Prussian Academy of Science in 1909.

Ludwig Mond was a man with a most impressive presence. He had a large head with a highly developed forehead. Although he was bald on the crown, his hair grew profusely round his neck and always evinced a tendency to curl. His eyebrows were thick and protruded somewhat over his dark, piercing eyes. His beard was full and his features generally were of an Oriental type. His face was capable of expressing extreme gentleness and intense severity. He had a keen appreciation of humour, and in his younger days was almost boyish in his mirth. He possessed a most sociable disposition, formed firm and lasting friendships, and ever preserved a tender regard for those with whom he had associated.

He possessed a sensitive and sympathetic nature, and was ever ready to assist those who were in trouble. He was a keen debater, but very quick in resenting obvious contradiction. The powerful will and firm self-confidence that enabled him to achieve so much made him disinclined readily to weigh other people's opinions against his own. A rapid thinker himself, endowed with a remarkable faculty for mental arithmetic, he was apt to become impatient with those who failed to follow. For him, all information had to be definite and precise; generalities annoyed him. He could not think of a problem unless he had volumes, weights, and temperatures to commence with.

His voice was deep and guttural, and he never so completely lost his German accent as to master the English "w's" and "th's." He possessed the power of obtaining sleep at will, and although an indefatigable brain worker, he could reinvigorate himself by taking half an hour of sleep, terminating almost at the moment he had arranged.

He was a great cigar smoker, and obtained stimulus from the practice. His consumption of a cigar kept pace with the working of his brain. When engaged in the discussion of abstruse problems,

he invariably walked up and down his room smoking, and as he became more and more absorbed in thought, his cigar burned faster and faster.

He was much beloved by his workpeople, who regarded him as an exacting master, but a perfectly just one. He could be, and often was, very angry with any man who was lazy or stupid, but he never kept any bitter feeling towards the delinquent. Much of his anger, too, was assumed for the purpose of making an impression.

During his absence in Rome in 1903, a report reached England that he had died, and obituary notices appeared in some of the newspapers. The news was quickly shown to be false, and on his next visit to Winnington the workpeople met him in torchlight procession, presented an illuminated address of welcome, and made Winnington Park gay with fireworks.

In 1898, to celebrate the twenty-fifth anniversary of the commencement of the works, Sir John Brunner and Dr. Mond presented a handsome building to the company to serve as a pavilion and recreation club for the workpeople. It was built in Winnington Park on the recreation ground. They further entertained their men with their wives and children, to the number of 12,000 individuals, at a *fête* in the park.

His winter residence in Rome developed that great love of the arts which had always been characteristic of him. He was intensely fond of music, and never so happy as when he could offer his hospitality to those who were celebrated in the art.

He was a great admirer of the early Italian painters, and he collected at his London house one of the finest galleries of their works in England. At his death he bequeathed these to the nation.

In an eloquent commemoration of their foreign member, Ludwig Mond, read to the Dei Lincei Royal Academy on April 3rd, 1910, by Raffaele Nasini, the author said:

"He loved Italy with a great love; he loved it on account of its brilliant skies, on account of its beautiful landscapes, the customs of the people, and its ancient art; he loved it in its men of science, in its men of literature, in its men of art. He assisted many provident and charitable institutions in this country; he relieved many disasters great and small, together with his good companion. Italians found in his hospitable house at The Poplars a piece of their own country, where everything spoke of Italy. How many glad remembrances of our country and our countrymen were evoked by Dr. Mond and his amiable family; how much admiration for Italy burst forth from their hearts whilst the Virgin of Tiziano and the beautiful Flora of Palmo il Vecchio were smiling on us.

"Italian science was a great favourite with Mond, and conspicuous grants were received from him by the Chemical Institute of Rome and my Institutes of Padua and Pisa.

"For our grand Cannizzaro he had an intense admiration and profound veneration. He said that his friendship with him was one of the greatest satisfactions of his life. In honour of Cannizzaro he founded in our Academy that conspicuous prize called after him, which will be delivered the first time in 1911, and let it be hoped that it will bear fruit equal to the love entertained for science by him who founded it. Last year (1909) the Italians who met in London for the International Congress of Applied Chemistry wished to show their gratitude to Mond, and on May 30th, in connexion with a splendid garden party given by Mond to the members of the Congress, there was offered to him, on behalf of nearly 500 chemists of our country, a bronze shield, the eminent work of our sculptor, Carlo Fontana, on which Mond's work was symbolised. On presenting it, speeches were made by Professor Ciamician, myself, and Professor Paternò, the latter expressing himself in very appropriate language as follows:

> "The prize you have founded and which you wish to adorn with the illustrious name of Stanislas Cannizzaro will be for Italian chemists, now and for ever, a perennial monument of their gratitude towards you. The honour shown to our grand master is an indissoluble link between your name and Italian Science.

Mond in his reply remarked that what he had had in view was to point out to the present and future generations of chemists what splendid results may be obtained from a life of true devotion to science such as had been, and was, that of Cannizzaro."

In addition to the portrait of Mond on the shield mentioned above, there are a marble bust (1896) by Joseph von Kopf, a bronze bust by Henri Glicenstein, a bronze statue (1906) by Ferdinand Seeboeck, a portrait medallion by E. Lanteri (1911), an oil painting by Solomon J. Solomon, R.A., and in Winnington Park stands a lifelike bronze statue by E. Lanteri, unveiled by Sir John Brunner in 1913 amid a remarkable concourse of Mond's old friends. Here, from his granite pedestal, wearing his well-known dust coat and patriarchal soft felt hat, holding a bundle of plans in his hand, the "Old Man" (as he was always called) stands looking at the works he loved so well. To one who sees this effigy daily, the thought often occurs: What would he think of them now? grown even beyond his plans; and a certain amount of satisfaction is derived from the fact that during all this remarkable development the statue apparently stands constantly watching.

Although some years have now elapsed since his death, it is not possible for the country to gauge the value of his work by noting

the size or number of the factories which he was instrumental in creating. The full benefit accruing from it will not be separately assessable from national industrial progress; but for a generation to come England will have reason to remember Ludwig Mond, the great pioneer chemical manufacturer. JOHN I. WATTS.

BENJAMIN HORATIO PAUL.*

BORN 1827; DIED 1917.

BY the death of Benjamin Horatio Paul, in his ninetieth year, there is removed one of the last of the Olympians of the early epical years of British scientific pharmacy. His life pilgrimage, so full of years and honour, was for a long space of its course contemporaneous with the history and progress of the Pharmaceutical Society, to the faithful and fruitful service of which he dedicated so rich a measure of his remarkable talents and energies. The late Dr. Paul was born in 1827, and in his fourteenth year entered the profession of pharmacy at Fakenham. He was one of the group of eight students in the Pharmaceutical Society's original laboratory during the first session of the School of Pharmacy, and in 1845, at the age of eighteen, won the school's first prize in chemistry and the second prize in organic chemistry. While a student in the school he came under the inspiring and formative influence of Pereira, that prince of teachers and master in pharmaceutical science and lore, with whom he formed a life-long friendship, and whose memory he cherished as one of his most precious possessions. Thereafter he studied at Giessen, under Liebig, and in 1848 took the degree of Ph.D. (Giessen). Returning to England, he prosecuted his studies under Graham (the Master of the Mint), acting as one of his assistants, and passed the Major Examination in 1852, the number of his Major certificate being 9. He first contributed to *The Pharmaceutical Journal* in 1846, and in 1856 commenced a notable monthly series of articles on "The Progress of Chemical and Physical Science," which succinctly and with characteristic accuracy summarised and reviewed the advances in these branches of knowledge. He was soon recognised as a leading authority on the pharmaceutical and allied sciences, to the advancement of which his original work then and later materially contributed. In particular, his researches in collaboration with Cownley on the chemistry of cinchona, ipecacuanha, and other alkaloidal drugs, have made permanent additions to the knowledge of these subjects, and his literary labours, which covered a wide scientific range, included contributions to the first edition

* Reprinted, by permission, from *The Pharmaceutical Journal*.

of Watts's "Dictionary of Chemistry," editorship of the English version of the German edition of Payen's "Précis de Chemie Industrielle" (1878), for which he wrote the supplementary chapters on the chemistry of the metals; the editorship for Bohn's series of Bolley's "Manual of Technical Analysis"; the Report, in collaboration with Passmore, of the First International Exhibition at Vienna in 1883; and, in conjunction with Holmes and Passmore, the Report on the Materia Medica Pharmaceutical and Chemical Industry Exhibits at the Paris Exhibition of 1878.

Dr. Paul was formally installed as Editor of *The Pharmaceutical Journal* in 1870, in succession to Bentley, Redwood, and Barnard, the triumvirate who had conducted it with somewhat divided counsels and policy from the time of Jacob Bell's death in 1859. From the outset of Paul's editorship the *Journal* became a weekly, and he soon introduced many of the distinctive features that it retained during the thirty-two years of his tenure of office, which witnessed many profound and pervasive changes in the internal structure and external environment of pharmacy, and consequently in the policy of the official organ of the Pharmaceutical Society. Some of these innovations were doubtless distasteful to a man who had breathed the atmosphere and been nourished on the generous aspirations and exalted ideals of the morning land of British pharmacy; and, for one of his perfervid intensity of conviction, it must have been increasingly difficult to subdue his mind and hand to a medium in which science had to compromise with business. He scorned, however, to palter with principle, as he conceived it, and during his long life, both in his editorial capacity and later, he staunchly and steadfastly held out for the prime necessity of the systematic and progressive education of the pharmacist as the only sound basis and sanction for his claim to professional recognition, and insisted on the practical value of a regular apprenticeship, as alike a preventive and cure of many of the more grievous evils from which British pharmacy suffers. In these respects the recent trend of events has amply justified his prescience.

Dr. Paul was an accomplished and versatile linguist, widely travelled, with an intimate knowledge of Continental life and thought, a brilliant conversationalist, an artistic *raconteur* of remarkable histrionic power, with a wonderful gift of playful or poignant wit, and was cast in the heroic, combative mould, with elements of sweetness and light in his composition which made him one of the most chivalrous and magnanimous of men, as ready to take a manly foeman to his arms as to break a lance with him. Dr. Paul touched life on many sides. His affinities with the modern spirit in literature and art brought him into sympathetic contact

and close communication with Dante Gabriel Rossetti and the protagonists of the pre-Raphaelite brotherhood, and Freemasonry as another aspect and manifestation of fraternity and fellowship strongly attracted him.

When Dr. Paul resigned the editorship of *The Pharmaceutical Journal* in 1902, although reckoned by the efflux of time he had exceeded the allotted span, he was still a man of vibrant vitality and unquenched spirit, and throughout his declining years had enjoyed wonderfully good health and an unabated zest of life.

RUFUS DANIEL PULLAR.

BORN JULY 6TH, 1861; DIED SEPTEMBER 22ND, 1917.

RUFUS DANIEL PULLAR was the elder of the two sons of the late Sir Robert Pullar. Born in Perth in 1861, he was educated, first at Sharp's Institute, Perth, and then at Craigmont School, Edinburgh. While still residing at Craigmont, he commenced to study chemistry at the University under Professors Crum Brown and Stevenson MacAdam. Here he made good progress, and at the completion of the course spent a year at his father's works in order to acquire a knowledge of practical dyeing.

In 1880 young Pullar entered the newly-created dyeing department of the Yorkshire College, now the University of Leeds, then in charge of the late Professor Hummel, with whom, indeed, he took up residence. He proved himself a hard-working and zealous student, and the University records state that he not only took the first prize and certificate in chemistry and dyeing, but also the highest honours and silver medal at the examination of the City and Guilds of London Institute in wool dyeing.

During the period of his stay in Leeds his kind and genial disposition found him many friends, and he enthusiastically entered into such sports as were then in vogue, being especially proficient in lawn tennis. He was, moreover, a clever photographer, and many prints are still extant from negatives taken by him during his year of studentship at Leeds. His interest in his old College and the subsequent phases of its development as part of the Victoria University and later as the University of Leeds, remained with him up to his death, and it was rarely he came to Leeds without visiting its dyeing department, so that he might discuss not only novel points of scientific interest, but also the possibility of methods for improving the study of his subject. His election in 1909 as a member of the Leeds University Textile and Dyeing Committee gave him much pleasure, and he often regretted that circumstances did not permit of his more frequent presence at its deliberations. It

was in 1882 that he took up the position of chemist to his father's firm, Messrs. J. J. Pullar and Sons, and now his real business career began. This well-known works was founded in 1824 by his grandfather, James Pullar, but its great development took place after 1848, when Robert Pullar, afterwards Sir Robert, became a partner. As chief chemist, Rufus Pullar continued until 1886, when he was received into partnership, and from that time forward his energies were so fully occupied in the development and enlargement of the business that his opportunities for actual chemical experiment became more and more limited. On the othe hand, his powers of organisation now came fully into play, and realising as he did the necessity of scientific methods, he spared no pains that these should be extended as far as possible throughout the factory. To further this object he visited foreign dye-works both in Germany, France, and America, and to these he had ready access, as a result of old family friendships which had originated with his grandfather. From its inception his firm, indeed, had closely watched each step in the advancement of the art of dyeing, and it was in these works at Perth that young Perkin, in conjunction with Robert Pullar, carried out the first experiments on any scale as to the application of mauve to fabrics. There are still in existence specimens of silk dyed with mauve at or about that time, much valued by both families, taken from a dress-length of heavy moiré silk which was presented to and graciously accepted by Queen Victoria.

As early as 1880 Pullar was elected a Fellow of our Society, and in the same year joined the Society of Chemical Industry. In 1883 he became a member of the British Association, at the meetings of which he was frequently present, and he indeed accompanied his father and uncle on its visit to Canada and the United States. His connexion with the Society of Dyers and Colourists dates from 1884, and of this in 1914 he became President, a position which he filled with distinction for two years.

From 1895 onwards Sir Robert and Mr. James Pullar, the older members of the firm, gradually withdrew from the actual management of the business, and as a result Rufus Pullar's active participation in scientific meetings, at no time an easy matter for him, owing to the distance of his home from their centres, was now considerably curtailed. Happy though he was in his own business sphere, in which, of necessity, his main interest centred, he never appeared better pleased than when in scientific circles, and there can be little doubt that he regretted that the exigencies of his position did not permit him actively to investigate some at least of the many theoretical problems which so frequently came to his notice. Whenever opportunity occurred, he spared no pains to emphasise the necessity

of a thorough scientific training for all those who were desirous of, or about to accept, positions of any responsibility in our factories, for, knowing the German methods so well as he did, he viewed with alarm the general neglect and lack of enthusiasm for science in this country. This was the tenor of his address to the Society of Dyers and Colourists in 1914, on which occasion he also pointed out that the chemist, to be thoroughly successful, should not specialise entirely in his own science, but should have also a general acquaintance with physics, engineering, and mathematics. In 1914 he accepted with much pleasure the invitation to join the Board of Trade Committee, then being formed to consider the methods of improving the dye industry in this country, and when, as a result of its deliberations, British Dyes, Limited, was founded, his interest in the matter was unceasing, and at times he visited the factory site to watch the developments there in progress.

As the head of the large and important business at Perth, Rufus Pullar was fully alive to his many responsibilities, and in addition to his desire for the continued success of the works, was keenly anxious, as, indeed, were his father and uncle before him, to devise methods for the greater comfort and social betterment of the firm's employees. Thoroughly businesslike and punctual in his habits, he expected the same from others, but, on the other hand, no calls on his leisure moments did he regret when these could be spent for the benefit of the community of his native town. Even with those who knew him intimately he rarely discussed his own concerns, and his quiet and unassuming manner gave little indication of his exceptional activity.

Although his business engagements were very exacting and his scientific interests absorbing, there are few, if any, of the numerous philanthropic institutions existing in Perth with which he had not been connected, either as president or in some position of active responsibility. He had always, indeed, been particularly attracted by public work, and he had hoped later on, as others came forward who could relieve him of his business cares, to devote himself to public life and, if possible, to enter Parliament.

At the outbreak of the war he fully recognised the necessities of the situation, and actively participated in the various local schemes which arose at this period of the national difficulty. Thus, when Lord Derby's recruiting scheme was started in 1915 he became a member of the Perth Advisory Committee, and this position he filled until March, 1916, when he was transferred to the Perth Appeal Tribunal. Later again, in 1917, he agreed to become the Sub-Commissioner for Industry in Perthshire, under the National Service scheme, the duties of which, arduous though they were, he took up with much enthusiasm, and was bitterly disappointed when,

as time went on, this movement proved a failure. In 1916 he assisted in the formation of "The Association of British Chemical Manufacturers," and although not a manufacturer himself, ultimately became a member of its Council. It is probable that the frequent journeys to London in connexion with this and the Association of Chemical Industry, together with the worry involved by the troublous crisis which had arisen in his own factory, overtaxed his strength.

He died in Edinburgh on September 22nd, 1917, after a short illness at the early age of fifty-six years.

Mr. Rufus Pullar married a daughter of the late Robert Morison, of Perth, who survives him. He leaves two sons, Mr. R. Morison Pullar, who is director and secretary of the firm, and Captain J. Lindsay Pullar, of "The Black Watch," who is serving in France.

A. G. PERKIN.

WILLIAM JAMES RUSSELL.

BORN MAY 20TH, 1830; DIED NOVEMBER 12TH, 1909.

IT is practically impossible to convey to a new generation any satisfactory impression of those features of a man's character and personality which were most apparent to his contemporaries. Hence it is of little use, and only for the satisfaction of those contemporaries, a rapidly dwindling company, that any reference is made to his genial presence, his characteristic hearty laugh, his sober and trustworthy judgment in business, and his quiet but persistent interest in matters scientific. Who he was and what he did can fortunately be set down with considerable accuracy and completeness, for documents remain which give all the necessary information. Few who knew Dr. Russell would have thought him likely to be one of those who not only made entries in a diary for the purpose of keeping engagements, but who set down every event in his own career from the age of fifteen to within a week of his death, and that all these memoranda should have been preserved.

William James Russell was born in May, 1830, and enjoyed the advantage of living under the care of father and mother during the whole of his early life, and therefore, although there is no record of his childhood, it seems certain that he received an enlightened kind of education. He went to two private schools, namely, Dr. Wreford's at Bristol and afterwards the Rev. Samuel Bache's at Birmingham. At this time, some idea of choosing for him the profession of engineering seems to have been introduced into the mind of his parents by several friends, and it was even

suggested that he should go as pupil to Mr. Beamish, a railway engineer. His father having been a good deal in Paris, had in 1801—3 attended the lectures of eminent men of science, particularly of the chemist Vauquelin, and it seems probable that the display of his interest in such subjects may have led the boy to think of the serious pursuit of chemistry as a life-long occupation. Moreover, he may have been influenced to some extent by tradition in the family concerning his father's, and especially his grandfather's, association with the famous discoverer of oxygen, Joseph Priestley. Whatever may have been the original source of the influence which ultimately determined his career, the diary reveals the fact that at the age of fifteen or thereabout he was not only attending various lectures on geology, botany, and chemistry, but was lecturing himself either to schoolfellows or friends, probably the latter, as the entries appear to have been made in the holidays. On September 23rd, 1847, the entry is "Left Birmingham for good," and on October 13th following, "Came to London," and next day, "Began to attend the classes." This was at University College, London, where he became a student of chemistry under Graham and Williamson.

Though doubtless a man's career is subject to much modification by the conditions surrounding his life, there is at least as much to be attributed to the bias which he receives from his ancestry; and before proceeding further, a glance may be appropriately taken at the history of the strange and eventful lives of his father and grandfather long before his birth. This has been provided in an interesting volume, "The Russells of Birmingham in the French Revolution and in America, 1791—1814," by S. H. Jeyes (George Allen and Co., 1911), which has been compiled from letters and especially from the diaries kept by Martha Russell, elder of the two aunts of William James.

Russell's grandfather, William Russell (1740—1818), was a contemporary and friend of Joseph Priestley, the famous divine and discoverer of oxygen. At the time of this discovery, William Russell was thirty-seven years of age, and must have felt considerable curiosity about his friend's work and its results, especially as, in a sort of way as guardian and warden of the Assay Office in Birmingham, he was presumably acquainted with some applications of such practical chemistry as were known in his day. But the tie of sympathy between the two men was rather political and religious, Russell being a member of the Unitarian congregation presided over by Priestley, and a substantial supporter of the minister, not only as a member of his congregation, but by furnishing liberal supplies of money. This association with so notorious a reformer, for

whom the High Church party of the day had no better name than "atheist" and "revolutionary," led to unfortunate consequences.

Public feeling in this country was exacerbated to a high degree by the outbreak of the French Revolution, and a series of disorders broke out in Birmingham, in the course of which Priestley's house was burnt and all his apparatus destroyed on July 14th, 1791, and the house of William Russell at Showell Green met with the same fate two days later. Priestley fled to London, and in April, 1794, he sailed for America and settled at Northumberland, a small town in Pennsylvania, where he died in February, 1804.

William Russell, though evidently a man of considerable courage and determination, having more than once confronted the rioters with remonstrances, was ultimately induced to seek a new home across the Atlantic. The story of the adventures of the father with his two daughters Martha and Mary and his son Thomas Pougher is recorded in the diaries of the elder daughter. To the volume already mentioned the reader must be referred for details, which, it must be said, possess more than a mere personal interest, as they throw much light on the state of parties in this country, on the condition of France during the Revolution, and on the social conditions prevailing in America. It is sufficient to say here that William Russell and his family started from Gloucestershire in July, 1794, and drove to Falmouth, where on August 13th they embarked. They had been at sea only a few days when they encountered a French frigate, and all the English voyagers were captured and taken to Brest. After some months they were released, and made their way to Paris, where they stayed until the following summer, when they sailed from Havre, and ultimately landed in New York in August, 1795. William Russell, ardent Republican though he was, found little to satisfy him in America, and in a few years the whole family returned to Europe.

Thomas Pougher Russell, the only son of William Russell, born February 3rd, 1775, was some years younger than his sisters, who were born respectively in 1766 and 1768. He seems to have found life in the new country less tolerable than did his more accommodating sisters. His father had purchased considerable property in France, and in 1801 he retired to his estate near Caen. Thomas spent a good deal of time in Paris, but there were difficulties about personal intercourse between father and son owing to the continuance of the war and the anomalous political position of the father. William Russell was admitted to the rights of French citizenship in 1807, and two years later Thomas also became a French citizen.

In 1813 Russell sold part of his French property, and advantage was taken of the peace which temporarily followed the internment

of Buonaparte in Elba for both father and son to return to their native country. No record exists of the terms on which Russell made his peace with the English authorities, but it is pleasant to know that he was spared to live four years in his native land. On January 26th, 1818, he died at the house of his son-in-law, James Skey, at Upton-on-Severn, aged seventy-eight, "a long suffering man who had met all his troubles with a cheery spirit and indomitable courage."

From the volume referred to, we learn that Thomas Pougher Russell maried in May, 1817, Mary, daughter of James Skey by his second wife, Eleanor (*née* Brockhurst), and had issue two daughters and one son, named after his two grandfathers William James. For the last thirty years of his life Thomas Russell was a banker in Gloucester, in partnership with James Skey and others. This private bank afterwards became the Gloucestershire Banking Company, of which he was a director. He also served for many years on the committee of the Gloucester and Berkeley Canal, and died in 1851 at Gloucester, of which city both he and his son were freemen.

As a student in University College, young Russell had the advantage of working under the most distinguished chemists of his time and of meeting with congenial companionship. Thomas Graham was the professor until his retirement on becoming Master of the Mint in 1855. At this time he was occupied with his famous studies of the phenomena of liquid diffusion. George Fownes was still professor of practical chemistry, but he died in January, 1849, and was succeeded by Alexander Williamson in October of that year. Russell's diary states that he began quantitative analysis in January, 1848, doubtless under the direction of Fownes, but as the diaries are missing for above a year at this time, there is no record of his associations with that brilliant man. On April 30th, 1850, "Heard that I had the medal for the Chemical Essay" is the entry. Other notes show that he went to hear Faraday lecture, and that on May 6th, 1850, he "went with Mr. Watts* to the Chemical Society to hear the discussion between Frankland and Hofmann about ethyl, amyl, etc."

Russell was not content with listening to discussions, for on the 29th of the same month, "Had a discussion at the Birkbeck Phil. Soc. whether Priestley or Scheele was the greatest philosopher. I spoke for Scheele; discussion adjourned." And again, in November, "Opened the discussion on the Dr.'s new theory of etherification at the Birkbeck Philosophical Soc." But all was not science and work, for there are many entries of dances and

* Henry Watts of Dictionary fame.

dinners, and especially of visits to theatres; among the last, November 11th, 1850, "Went with Frank and Henry Roscoe to the Olympic Theatre to see Miss Faucit," etc. This was the end of his student time at University College, for in January, 1851, Frankland, who was then at the College of Engineering at Putney, offered him the post of assistant at Owens College, Manchester, then about to be opened, and where Frankland had been appointed the first professor of chemistry. On February 8th, 1851, his father died, and naturally this event took him away from his work for a time; but by the end of the month he was in Manchester assisting Frankland with his lectures, the introductory lecture being given on March 20th. Here Russell remained until 1853, when he decided to go to Germany.

July 1st: "The laboratory students met and presented me with a copy of Tennyson's works as a parting gift, a most pleasing and unexpected thing to me."

The choice of the laboratory at Heidelberg, where Bunsen was professor, was determined on before the end of the previous year, for a letter from Roscoe dated December 14th, 1852, contains the following passage: "I am glad that you think of Heidelberg first, because I have a great desire to go there too, and I am sure Bunsen must be a capital man." Early in September Russell arrived at Heidelberg, and on the 7th "Harry Roscoe and I went to see the laboratory, a curious old place very different from the Owens College one." Among his fellow-students were, besides Roscoe, Ronalds and Matthiessen, Lothar Meyer, Edmund Atkinson, Pauli, Hermann, and Meidinger. Experiments on paraffin, which he had begun at University College, were carried on for a time, but soon Bunsen suggested other work, and on December 16th, 1854, the diary reports, "Took my degree." Whether the subject of his thesis was the composition of the gases produced in flames or the research on a method of estimating sulphur in volatile compounds (published in the *Quart. Journ. Chem. Soc.*, 1854, **7**, 212) is uncertain. He seems to have remained at Heidelberg until the following August, when he returned to London.

After various disappointments and tentative experiments in connexion with industrial applications of chemistry, Russell became teacher at the Midland Institute, Birmingham, and gave a short course of lectures in June, 1857. This summer the professorship at Owens College, Manchester, fell vacant by the removal of Frankland to London. Russell became a candidate, but his friend Henry Roscoe, his senior by three years, received the appointment. Russell returned at the end of the year to University College, and on December 7th "went to the laboratory, saw Williamson, and

he explained his gas apparatus to me; the thing is altogether in an impracticable form." This, however, was followed by a long investigation, which resulted in two papers jointly with Dr. Williamson (*Proc. Roy. Soc.*, **9**, 218; *Journ. Chem. Soc.*, 1865, **18**, 238), and two others independently, on gas analysis and on the application of the measurement of gases to quantitative analysis (*Journ. Chem. Soc.*, 1868, **21**, 128, 310). While this work in the laboratory was going on, Russell conducted the evening classes in chemistry at the college, and gave a course of practical chemistry in the school. During the first session of the Albert Veterinary College, he gave the course of lectures on chemistry, and in July, 1860, was appointed lecturer on natural philosophy at the College for Ladies, Bedford Square (Bedford College). He was now pretty fully occupied with teaching, but it did not prevent activity in other directions. He had attended several meetings of the British Association, and at the Oxford meeting in 1860 Russell took a leading part in the foundation of the famous dining club, known as the "Bs." An interesting account of some of its proceedings was given in Dr. Scott's Presidential Address, March, 1916 (T., **109**, 342). The diary tells us that the rules of the club were drawn up on July 23rd, "the first meeting of our dining society" was on November 6th, and another meeting took place at the Cheshire Cheese on December 4th.

In October, 1861, Russell became engaged to Fanny Follett Osler,* a daughter of Abraham Follett Osler, the well-known glass manufacturer, of Birmingham. They were married on August 21st following, and took up their abode at 8, Circus Road, St. John's Wood. In 1865 he was appointed lecturer at the Royal Albert Veterinary College, and in the following February he bought the house 34, Upper Hamilton Terrace, which remained his London home to the end.

In 1868 Russell was appointed to the post of lecturer at St. Mary's Hospital, previously occupied by Matthiessen, and his activity may be estimated by recalling the facts that during the seven or eight years immediately previous to this time he had continued his teaching at University College and at Bedford College. He also attended meetings of the British Association, and on the last two occasions had served as one of the secretaries of the Chemical Section. He worked assiduously at gas analysis, and in conjunction with Williamson published several papers on the subject in the Proceedings of the Royal Society and in the Journal of the Chemical Society. He had also investigated jointly with Matthiessen the important question as to the cause of the

* She died on May 15th, 1871, leaving a son and a daughter.

vesicular structure of copper. They showed that this phenomenon is observed when copper is melted under charcoal only when oxygen or air is passed through the metal, and they inferred that the peculiar structure could only be attributed to the formation of carbonic oxide arising from the reduction of cuprous oxide within the mass by charcoal. The cavities in the metal are always untarnished, and hence cannot contain any oxidising gas. In 1863 he had communicated to the Chemical Society some important work on the atomic weights of cobalt and nickel, and was led to the conclusion that they are practically identical, the value found for Co' being 29·370, whilst that for Ni' was 29·369. The method consisted in the reduction of the protoxides by hydrogen and determination of the weight of the resulting metal. In 1869 he published further experiments, in which the same metal used in the former work was dissolved in dilute hydrochloric acid, and the evolved hydrogen was measured. The results were practically the same, and the atomic weights of the two metals were consequently supposed to be represented by the same number, namely, 29·3 or thereabouts. This was in accord with the view prevalent fifty years ago, even after the discovery of the periodic law. The problem presented by these two closely allied elements, however, attracted a large number of chemists, and the idea of the identity of their atomic weights has had to be abandoned. This may perhaps be partly attributed to advance of knowledge as to the properties of the two elements, including the discovery of nickel carbonyl, the decomposition of which affords a means of separating that metal completely from all other substances. There can be no doubt now that the atomic weight of cobalt is greater than that of nickel, and practically in the ratio given in the International Table of Atomic Weights, namely, Co : Ni : : 58·97 : 58·68, when $O=16$. These values agree with the result obtained by comparing the specific heats, namely, 59·01 : 58·70. At St. Mary's Hospital, Russell remained about two years, but in December, 1870, he was appointed to the lectureship at St. Bartholomew's, left vacant by the unhappy death of his friend Matthiessen. A new laboratory had been very recently built and had been ready for occupation at the commencement of the session in October. Here Russell continued his work until he retired from all teaching in 1897.

A word may here be said on the subject of Russell's qualities as a teacher. He was wise enough to perceive that the course of elementary chemistry usually followed was unsuitable for medical students without modification, and the change he introduced undoubtedly affected the course of instruction in other medical schools

and the syllabuses of examinations, such as those of the Conjoint Board. All this led to great improvement in the attitude of the students of medicine toward the chemical subjects, for whereas there had been previously not only reluctance to attend, but frequent disorder, they soon recognised the sympathy of their present teacher, and there was little, if any, trouble during his connexion with the school. The diary gives evidence on this point, for on January 11th, 1871, the entry is: "Gave my first lecture at Bartholomew's; went off all right," and on the 14th: "Lectured again; students perfectly quiet." As to other difficulties consequent on the many changes which about that time arose not only in the requirements of the medical curriculum, but also in the working of the School itself, we have the testimony of Dr. Samuel West, who was then working in the laboratory with Russell, that they were met "with invariable good humour, willingness, and courtesy." He seized the opportunity of becoming President of the Chemical Society to deliver in 1890 an address setting forth his views on the teaching of chemistry to students of medicine. These were inspired with his characteristic good sense. But it was not only in relation to medical students that his interest and sympathy were engaged. He had great experience as a teacher of elementary chemistry and physics to young people, both at University College School and at Bedford College, and after retirement from the lectureship at the latter institution he became chairman of the Council and took an active interest in the development of the College. Part of his success as a teacher and examiner probably arose from the habit of his mind, which was more attracted by facts and phenomena than by theories concerning them. He was certainly not one of those who delight in the manufacture of hypotheses, and all his own work and teaching were directed by unaffected good sense and clear judgment.

In 1872 Russell was elected F.R.S. He was elected into the Royal Society Club on June 26th, 1879. In 1873 he was president of the Chemical Section of the British Association at Bradford. His address was chiefly devoted to the very appropriate subject of alizarin, the history of the discovery of its constitution, and of the then recent synthetical production of this important colouring matter.

The *Journal* of the Chemical Society contains, in January, 1874, a very interesting paper on the action of hydrogen on silver nitrate, in which it is shown that hydrogen passed into a silver nitrate solution causes the deposition of metallic silver in quantity equivalent to the hydrogen which is absorbed, provided the solution is prevented from becoming acid by introducing a small quantity of silver

oxide. If the liquid becomes acid in consequence of the displacement of the silver, nitrous acid is formed and the reaction becomes more complicated.

About the same time experiments had been going on in his laboratory on a method of estimating urea in urine for clinical purposes, and in August, 1874, the *Journal* contains a paper on the subject published jointly with Dr. S. West. The method was based on the action of hypobromite on the fluid and measurement of the evolved gases. This was followed up in the wards of the hospital, and in 1880 the authors published their results in the *Proceedings* of the Royal Society (No. 204, 1880).

Various other researches were carried on, and at the same time Russell became involved in several technical inquiries which took up practically all his spare time. In 1875 he was also appointed one of the examiners in chemistry to the University of London. His colleague for some time was Roscoe, and naturally the London man got his full share of the work and the attendances at examiners' meetings. In 1876, also, the movement began within the Chemical Society which resulted in the formation of the Institute of Chemistry, and Russell's attendance at several initiatory meetings is recorded in the diaries. He became president of the Institute in 1893, and served for three years. About this time the subject of absorption spectra attracted his attention, and he spent much time working with Professor Lockyer at South Kensington. The result was a paper in the *Proceedings* of the Royal Society, 1880, on the absorption spectra of cobalt salts. But more important results were published (in conjunction with W. Lapraik) the next year on "Absorption Bands in the Visible Spectrum produced by Certain Colourless Liquids." Hartley and Huntington had already studied the absorption in the ultra-violet (*Proc. Roy. Soc.*, 1880, **28**, 233), whilst Abney and Festing had observed the absorption in the infra-red end of the spectrum produced by colourless liquids (*Proc. Roy. Soc.*, 1881, **31**, 416), but the visible portion of the spectrum had not previously been examined, and the discovery of bands in this part of the spectrum produced by the alcohols and colourless hydrocarbons has led to a vast amount of work by others since that date. The study of absorption spectra interested Russell very much, and there was another paper, also in conjunction with Lapraik, in the *Journal* of the Chemical Society (1882) on chlorophyll," but, as he himself stated, the expectations which had been raised and the hopes entertained when absorption spectra began to be studied were not then fulfilled; nor can it be said that they have been since. This, however, cannot be regarded as an argument against carrying on such investigations; rather the

contrary, for inability to deduce definite conclusions merely indicates a state of imperfect knowledge.

All kinds of problems which possess a direct practical interest or value always attracted Russell, and this led him to devote a great deal of time to the examination of the air and rain of London. St. Bartholomew's Hospital Report (Vol. XX.) contains a record of work done in 1882–3 on the carbonic acid in London air, whilst the Meteorological Office Report for August, 1885, gives the results of a laborious inquiry into the nature and amount of the impurities, solid and gaseous, in London air.

Another subject which occupied much time and attention was the study of the action of light on water-colours undertaken in conjunction with Sir William Abney at the request of the Science and Art Department in 1886. The first report was issued two years later, and contains an elaborate scientific discussion of the nature of colour and the constitution of various lights to which water-colours are exposed, as well as the influence of moisture and air and the extent of the chemical changes observed. The conclusions to which the investigators came may be briefly summarised in the statement that mineral colours are far more stable than vegetable colours, that moisture and air together are essential to the production of change, and that it is the blue and violet components of white light which are chiefly concerned in bringing about fading in the pigment. One of the difficulties of the inquiry arose from the fact that one of the main objects of the investigation was to ascertain what changes water-colours would be liable to if exposed to usual indoor conditions during at least an ordinary working lifetime. Fortunately, twenty-six of the colours originally subject of inquiry had been preserved by Mr. T. H. Russell in his father's house, and in 1914 they were examined by himself and Mr. Edwin Bale, R.I. The results of their examination are recorded in the *Journal* of the Imperial Arts League, and have been reprinted in the form of a pamphlet, which has been published by Messrs. Winsor and Newton, Ltd., so that artists can select for themselves the colours which are known to be the most durable.

An inquiry of cognate character was directed as to the state of the Raffaelle Cartoons at South Kensington. This Russell reported on in July, 1891. Ancient Egyptian pigments were also the subject of a lecture he gave at the Royal Institution in March, 1893.

It is time, however, to refer to his long connexion with the Chemical Society, of which he was elected a Fellow on March 3rd, 1851 (before he was twenty-one years of age), and of which forty years later he became president. Absence in Germany and at Manchester sufficiently accounts for the fact that the diaries give no evi-

dence of his attendance at the meetings for several years after election, but from 1857 onward he seems to have attended frequently in every year without a break down to the year of his death. In 1863 he first joined the Council, and thereafter he was an active member of various committees connected with the Society. He was elected Treasurer in 1876, and held that office until elected President in 1890. The great event during his occupation of the chair was the celebration of the jubilee of the Society, in 1891. As President, Russell took the chair at the dinner on February 25th, 1891, and the occasion was distinguished by the presence of the Prime Minister, Lord Salisbury. The diary characteristically reported that "it went off very well."

A series of experiments undertaken with the object of repeating Becquerel's observations on the photographic effects produced by compounds of uranium resulted in the remarkable discovery that zinc and a number of other metals produce a similar effect. The first announcement of the fact appeared in the *Proceedings* of the Royal Society for 1897. And the prosecution of the work led to the further discovery that not only metals, but varnishes, printing ink, and a variety of organic substances share this property. The results were collected in a second paper, which formed the Bakerian Lecture for 1898. The effects were soon traced to the formation of hydrogen peroxide, and in March, 1899, a third paper was communicated to the Royal Society under the title "Hydrogen Peroxide as the Active Agent in producing Pictures on a Photographic Plate in the Dark." One remarkable point brought out in these experiments was the exceedingly minute quantity of the agent which was competent to produce the effect. The inquiry was pursued for some years, and the effects on a photographic plate produced by sections of various woods provided a fascinating subject, which was developed with many beautiful illustrations and communicated to the *Philosophical Transactions* for 1904. Two later papers described the effect produced by leaves and other parts of plants, also by resins. In 1897, Russell had resigned the office of lecturer at St. Bartholomew's Hospital, which he had held for so many years, and after this time his experimental work was done at the Davy-Faraday Laboratory. Here, also, he carried out the experiments on the "Formation of Definite Figures by the Deposition of Dust," which were published in the *Philosophical Transactions* for 1903. An explanation on physical principles of the formation of these curious deposits was soon afterwards given by Mr. J. Aitken, F.R.S. (*Proc. Roy. Soc.*, 1904, **72**, 211).

Russell was elected under Rule II a member of the Athenæum Club on February 26th, 1889. The rule provides for the annual

introduction of a small number of "persons of distinguished eminence in science, literature, or the arts, or for public services." A few years later Russell became a member of the Committee.

Russell delighted in the country and in all sorts of natural objects and in scenery. He had travelled a good deal on the Continent of Europe, but his own country supplied him with all the enjoyment he needed in his latter years. And he was a most genial host. For many years, from about 1882, he had a house on the edge of Dartmoor, Scorhill, near Chagford, and there he delighted to show his visitors the views of sunsets over the moor or the curiosities of form among the tors. Notwithstanding its attractions, the difficulty of access to this retreat led to a removal in 1897 to St. Ives, near Ringwood, Hants, a house surrounded by beautiful plantations, including extensive rhododendron avenues. Here he entertained frequent visitors, and the annual excursion into the neighbouring New Forest at Whitsuntide was an event for pleasant anticipation. It was delightful to accompany him in visiting his favourite trees in his own grounds, and to share the evident enjoyment with which he discoursed about their history or peculiarities.

In August, 1909, he left London as usual, and went to St. Ives. He had, however, been failing in physical strength for some time, and though in the early part of the summer he had dined out several times, there is an entry in the diary on July 18th, "Taken ill," and on August 10th, "Went to Ringwood." Here, after a short illness, during which he was unconscious, he passed quietly away.

W. A. T.

FRANCIS SUTTON.

BORN FEBRUARY 19TH, 1831; DIED APRIL 16TH, 1917.

THE name of Francis Sutton is known throughout the chemical world by reason of his authorship of "A Handbook of Volumetric Analysis," which has been recognised as the standard work on the subject for the past fifty years. Ten editions of the work were published during the author's life, and each edition has kept well abreast of the current work in this branch of analysis. Sutton contributed but little original matter to analytical chemistry; his strenuous life and professional engagements never allowed him time for development in this direction, although his natural ability and grasp of the science might, in other circumstances, have enabled him to become a great chemist.

Francis Sutton was an only son, born on February 19th, 1831, at

Great Plumstead, a village near Norwich, Norfolk. His father, Francis Sutton, was a small farmer and farrier with a local veterinary practice. The son received his earliest education at the village school of Blofield, two miles distant from his home, and later attended a private school in Norwich, riding daily the ten miles to and fro by pony.

At the age of fourteen young Sutton was placed with a Mr. Harper, a druggist, of Norwich, with a view to acquiring some knowledge of drugs and chemicals prior to being sent as a student to the Veterinary College in London, for his father intended the boy to become a veterinary surgeon. The study of materia medica, botany, and chemistry was found so interesting that with his father's consent he was apprenticed to Mr. Harper and remained with him as assistant until 1851.

Then, at the age of twenty, Sutton decided to join a former fellow-apprentice who had started a druggist's business in West Clayton Street, Newcastle-on-Tyne, and it is of interest that the journey to the northern town was made by sea in a small coasting vessel from the now dead port of Blakeney on the north Norfolk coast. Thus he was brought into contact with a then growing centre of chemical industry and study, and while practising pharmacy had opportunity of becoming acquainted with men interested in pure and applied chemistry, among others Joseph Wilson Swan and John Pattinson, who remained life-long friends. A Dr. Glover, a physician of Newcastle, who devoted a good deal of time to medical chemistry and analysis, and subsequently became physician to the Royal Free Hospital, London, took much interest in the young pharmacist of West Clayton Street, lending him books, employing him in various chemical experiments as an assistant, and advising him to take up seriously the study of scientific chemistry. As a result of this help and encouragement, Sutton, in such time as was available, attended the lectures and worked in the laboratory of Dr. Richardson, then lecturer in chemistry at the Newcastle College of Medicine—at that early date associated with the University of Durham, and later known as the University of Durham College of Medicine. It was, however, through Dr. Marreco, then assistant to Dr. Richardson, that he received his main instruction in the theory and practice of chemistry, and laid a firm and sure foundation for his subsequent interest and achievement in that science. He must have been an apt and earnest pupil, for, as junior partner in the druggist business, most of the day was fully occupied, and his lectures and laboratory work had to be snatched at odd hours.

His residence in Newcastle and the opportunity for instruction

came to an abrupt end in November, 1854. His old master at Norwich was dying, and an urgent appeal was made to Sutton to return to Norwich and manage the business in which he had served his apprenticeship. He did so, and settled in Norwich, carrying on the pharmaceutical business in partnership with his late master's widow, and subsequently alone, until growing interests necessitated taking a partner. Meanwhile his keen interest in chemistry and chemical analysis was maintained, and led to part of the business premises being converted into a laboratory. At this period the work of Lawes and Gilbert at Rothamsted in the use of artificial fertilisers was beginning to receive the attention of agriculturists, and Sutton turned to the study and analysis of fertilisers. By advocating the new ideas among local farmers and advising and helping them, he established the nucleus of an analytical and consulting practice, which quickly developed.

In 1870 he originated and became managing director and partner in a chemical manure works at Runham, Great Yarmouth (Baly, Sutton and Company, Ltd.), where the manufacture of sulphuric acid, hydrochloric and other acids, as well as superphosphates, chemical manures, and sulphate and chloride of ammonia was carried on. The works and business were disposed of in 1893 to Messrs. Prentice Brothers, Ltd., of Stowmarket.

While at Newcastle in 1853 Sutton had become a member of the Pharmaceutical Society, and in Norwich his ability as a pharmacist was quickly recognised. He was elected to the Council of the Pharmaceutical Society in 1870 and continued to serve until 1876, when he finally abandoned pharmacy and disposed of the business to his then partner—in order to devote his time to his consulting and analytical practice and other interests. While serving on the Council of the Pharmaceutical Society he was chosen as one of the two delegates to represent Great Britain at the International Pharmaceutical Congress in St. Petersburg in 1874, and was afterwards elected a corresponding member of the Imperial Pharmaceutical Society of that city and also of the Apotheker Verein of Vienna.

Sutton's earliest contribution to scientific literature was in the form of two papers, published in the *Chemical News* in 1860, on the volumetric determination of phosphoric acid by uranium. In 1862 the first edition of his "Volumetric Analysis" was published; it was a small volume of 273 pages; the second edition followed nine years later in 1871, and was much more ambitious and comprehensive. Professor H. McLeod contributed a section on gas analysis, and the late Mr. William Thorp contributed to the section on water analysis. The latter, by advice and correction of proofs, gave acknowledged assistance in many subsequent editions.

The fourth edition was translated into French by the late Dr. C. Méhu and published in Paris in 1883. In all, ten editions were published in Sutton's lifetime, the last being edited by his son, W. Lincolne Sutton, and A. E. Johnson.

The period of life between 1860 and 1876 was an exceptionally full one, for Sutton, while carrying on simultaneously a very successful pharmaceutical business, had established and developed a considerable analytical and consulting practice, published the first and larger subsequent editions of his book, and had founded and was managing the chemical works at Yarmouth He had been appointed analyst and consulting chemist to the Norfolk Chamber of Agriculture, public analyst for the County of Norfolk and Borough of Great Yarmouth, and gas examiner to the City of Norwich. For many years he was in considerable demand as an expert witness before Parliamentary Committees and in the Law Courts.

Francis Sutton undoubtedly possessed great natural ability and versatility and had wide interests. In his prime he was a strikingly handsome man, with finely moulded head, aquiline nose, full beard, and ruddy complexion. His generous nature, sociability, and love of "good company" endeared him to a wide circle of friends; another personal trait was his beautiful handwriting. He took an active part and held office in various local scientific and other societies, such as the Norfolk and Norwich Geologists' and Microscopical Societies (both now extinct), the Norfolk and Norwich Naturalists' Society, of which he was at one time president, and he was an original member of the Norwich Science Gossip Club. He was a great lover of music, and possessed considerable knowledge of classical and operatic music. He was an active member of the Norwich Philharmonic Society for over forty years, and played the clarinet and later the oboe in the orchestra. He served for many years on the general committee and committee of management of the Norfolk and Norwich Triennial Festivals. He was an omnivorous reader of catholic taste, and served for many years on the committee of the Norfolk and Norwich Library, some time as president. Throughout his long life his chief outdoor recreation was fishing, a sport in which he took general interest. He was appointed a juror to the original Fisheries Exhibition held in Norwich in 1881 and also in the International Fisheries Exhibition of 1883 held in London.

Francis Sutton married in 1859 Marianne Harriett, the youngest and eleventh child of William Lincolne of Halesworth, Suffolk, and had issue seven children, three sons and four daughters, all of whom lived to maturity and married. F. N. S.

WILLIAM HENRY SYMONS.

Born November 16th, 1854; Died August 25th, 1917.

The ranks of the Public Health Official Service suffered the loss of a most capable and enthusiastic member by the death, on August 25th, 1917, of Dr. William Henry Symons, for twenty-one years Medical Officer of Health of the City of Bath.

Born on November 16th, 1854, Dr. Symons, a native of Dunster, first adopted chemistry as a vocation, and becoming chemist to Messrs. Idris and Co., aerated water manufacturers, of Camden Town, rapidly acquired a considerable practice as a consulting chemist. During this period he became a member of the Chemical Society in 1874, Fellow of the Institute of Chemistry in 1888, and published various papers, among them being: "A new method for the detection of various starches," "The detection of sodium in lithium carbonate," "Ulexine, an alkaloid from the common furze," "The difference between ulexine and cytisine," and a paper in the *Transactions* "On the volumetric determination of carbon dioxide in the atmosphere." His inclinations were, however, towards the application of chemistry to medicine, and entering St. Bartholomew's, he obtained the M.R.C.S. and L.R.C.P., and the M.D. Brussels in 1894, and the D.P.H. of Oxford and Durham in the following year. During this period he acted as assistant demonstrator in materia medica, was examiner under the Pharmacy Act, published papers on "Ipecacuanha," and edited the "Year Book of Pharmacy." For a short time he acted as Medical Officer of Health to St. George's, Southwark, and was appointed to the City of Bath in 1896. During the twenty-one years in which he held this post, he inaugurated a completely new régime with regard to the municipal health department, and his elaborate reports on the health of the city were greatly valued by the Corporation. His work in connexion with child welfare at Bath "brought this branch of public health work to a high standard of efficiency, and his efforts to secure a thoroughly satisfactory midwifery service in the city, embodying the provision of the Municipal Midwives Act, were fruitful of good results." For some years he was a member of the council of the Society of Medical Officers, and president of the West of England branch in 1911.

His interests were wide: he had made a special study of town planning, and in this connexion frequently visited the Continent; he also took an active part in the organisation of the Wensley Sanatorium, near Bath, for tuberculosis. One of his hobbies was

meteorology, and it was through his energy that the meteorological department at Bath was modernised, several stations equipped, and for the first time a series of careful observations recorded. This was obviously of value to a city famous as a health resort, and led to his appointment as City Meteorologist and a member of the Committee of the British Association appointed to investigate the effect of climate upon health and disease.

He was a well-known member and fellow of the Royal Sanitary Institute, and contributed to their *Journal* and discussions. Among his contributions, not previously mentioned, were the following: "Cancer in relation to the dwelling," "Ventilation," "The life-history of *Musca domestica*" (and it may be mentioned that he was a pioneer in the crusade against the fly danger), "Flies and refuse heaps," "Distribution of phthisis."

In the obituary notice in the *Journal* of the Royal Sanitary Institute, one of his friends wrote as follows: "One of his most striking personal qualities was his great enthusiasm in whatever he undertook . . . no one who was brought into intimate relationship with him ever harboured any unkindly sentiment towards him. The golden qualities which made him a model husband, father and friend, were somewhat cloaked by an excessive natural reserve, but these qualities were bountifully disclosed to many friends and colleagues who mourn his loss and who will be inspired by the memory of his friendship, and the earnest endeavour which secured for him the reward of much good work accomplished in the sphere of public health." F. F.

THOMAS TYRER.

Born November 17th, 1842; Died February 21st, 1918.

The sudden death of Mr. Thomas Tyrer, which took place at his residence, 14, Sandswell Mansions, Hampstead, on Thursday, February 21st, is already generally known to the chemical world at large, and it came as a great shock to such intimate friends as the writer, who had the privilege of being one of his closest friends and was associated with him both in business and private life for some twenty-nine years.

Although of good age, there was a fair prospect of further years of useful life, but the death of Mrs. Tyrer and a recent operation for cataract evidently affected his health and tended to hasten the end.

As one who was treated by Mr. Tyrer as a son or younger brother, the writer feels that (beyond the great loss sustained by chemical industry) the world has lost a good man—one who was generous and good-hearted, always ready to acknowledge and help forward others, even at the expense of himself. Although somewhat hasty in temper (like many other great men), Mr. Tyrer never knowingly allowed his feelings to injure or hurt anyone, and as a friend and adviser would spare no trouble or expense to render the very best possible help, his help being by no means confined to those who could claim strong personal friendship. In business he was generous to all who in any way showed themselves faithful and earnest, and he had no sympathy with those who believed that in business the great and strong are justified in "ousting" the smaller and weaker man.

He was able quickly to grasp the salient points and master the details of any matter placed before him, and his sound reasoning and extensive and general knowledge made him a valuable counsellor, whilst he was also possessed of great diplomatic ability. Had he turned his thoughts towards political life he would doubtless have become one of the leading men in the government of the country.

As has already been mentioned in the various trade journals, Mr. Tyrer's connexion with commercial and industrial chemistry extended over some fifty-five years. He was born at Wolverhampton in 1842, and received his education from his father, who was a schoolmaster, from whom he also acquired his habit of fearlessly speaking the truth to all and in all circumstances where necessary.

He was apprenticed to a manufacturing chemist named Wildsmith at the age of fifteen, and he entered the Royal College of Chemistry in Oxford Street (now incorporated in the Imperial College of Science) in 1861, and studied here under Hofmann, his experience with whom and with his fellow-students being always a favourite theme for conversation.

He also studied biology under Huxley and physics under Tyndall, but owing to the condition of his finances he had to relinquish these studies and became technical manager to Messrs. May and Baker, of Battersea, of which firm he subsequently became a partner.

Meanwhile, he was acting as honorary lecturer in chemistry to a working man's institute. His partnership with Messrs. May and Baker terminating in 1889, he, on January 1st, 1890, acquired from Messrs. Dunn and Co. the Stirling Chemical Works, Stratford, which in 1898 was formed into a limited liability company

(Thomas Tyrer and Co., Limited); of this he became managing director, and held this position at the time of his death.

In 1912 he undertook the manufacture of cellon aeroplane dope, and on the outbreak of war in 1914 he was able to extend and keep pace with the demand. Later on, by the erection of one of the best equipped factories, he added largely to the output, and was able to cope with the continually increasing requirements of the Government, due to the war.

Outside his business, some of the widest known work he did was in connexion with the duty-free alcohol question and the foundation of the Society of Chemical Industry. As chairman of the Chemical Trade Section of the London Chamber of Commerce, he, in conjunction with David Howard, Charles Umney, and others, took part in obtaining the grant of duty-free spirit for medicinal and other alcoholic preparations to be sent abroad, and thus enabled English manufacturers to compete with the foreign trade in these products.

He was also successful as a member of the Industrial Alcohol Committee in obtaining the reduction of the quantity of wood spirit used in denaturing alcohol (for use in manufacture) from 10 to 5 per cent.

In connexion with the Society of Chemical Industry, which was really instituted by a meeting of chemists convened by Mr. Hargraves at Widnes in 1879, and subsequent meetings at Widnes, Liverpool, and Manchester (known first as the Widnes and Runcorn Chemical Society, and later as the Lancashire Chemical Society and the Society of Chemical Engineers), Mr. Tyrer was most active, and may be said to have been one of its principal founders. In April, 1881, a meeting was held at Burlington House, at which Mr. Tyrer, with G. E. Davies, Roscoe, Abel, Ludwig Mond, Spiller, and other famous chemists took a most prominent part, Mr. Tyrer suggesting that the society be called the Society of Chemical Industry, and this suggestion was adopted in spite of opposition. He was honorary secretary of this society for ten years, chairman of the London Section 1890—1892, president 1895—1896, and honorary treasurer from 1908 (after the death of Mr. Hall) to the date of his death.

During the whole time he served the council in every direction, and his energies in this connexion aided materially in bringing the society from a small beginning to one of the largest, the members now numbering from four thousand to five thousand. That his great efforts in the chemical industry were recognised is shown by the fact that he had many honours conferred upon him, amongst

which may be mentioned the award of a silver salver and purse of gold by the Society of Chemical Industry under the presidency of Sir Fredk. Abel in 1891, the medal of the society in 1910, and in connexion with the industrial alcohol question a silver tea and coffee service in 1905.

One might go on indefinitely describing the work of such an energetic worker as Mr. Tyrer, but the greatest thing of all is the character he leaves behind, which cannot be better expressed than by quoting Professor Henderson's recent words.

"Kind-hearted and generous; a steadfast friend and chivalrous opponent; a wise and cautious counsellor; a benevolent helper of many a young and struggling man; an earnest advocate of every cause which he believed to be right and good; eminently sociable, a lover of music, a lover of talk in congenial company—such was Thomas Tyrer. It will be long before his memory fades."

Mr. Tyrer died as he wished, "in harness," and, as Professor Henderson says, it will be long ere his memory fades, especially amongst those who knew him well and recognised his real worth.

T. Tucker.

REGINALD COWDELL WOODCOCK.

Born December 11th, 1851; Died January 5th, 1918.

Reginald Cowdell Woodcock received his early education at two private schools, and subsequently (1866–1867) attended King's College School, London, taking the regular course in French, German, drawing, chemical physics, etc.

During 1867–1868 he was employed in Paris by the London Warming and Ventilating Co., assisting his father in a series of experiments in the Pantheon, preparatory to the introduction of heating the buildings by means of the "Gurney" stoves. He frequently visited Paris after that time, and was there when the Revolution broke out, followed by the removal of Napoleon III.

Having attended some lectures at the Royal College of Chemistry, he joined as a regular student in 1869, passing the examination in June, 1870, when he obtained a first class certificate and the "Special Certificate" for research work, "On the Action of Normal and Acid Salts upon Ammonium Salts, especially upon Ammonic Chloride," published in the *Journal of the Chemical Society*, 1871, **24**, 785, also in Watt's "Chemical Dictionary," 2nd Suppl., p. 60. In October, 1871, he became private assistant to Dr. Frankland at the Royal College of Chemistry, and was engaged in that capacity

on chemical analyses and research work, one lengthy investigation being for the Russian Government in respect of the destructive distillation of various woods and the possibilities of making use of the gases produced therefrom for illuminating purposes.

He was elected a Fellow of the Chemical Society in December, 1871. In January, 1872, he was appointed chemist to the Bede Metal and Chemical Co., Ltd., Jarrow-on-Tyne. In March, 1873, he received the appointment (following his friend, the writer) as assistant professor of chemistry at the Royal Agricultural College, Cirencester, where he remained until 1878. During his stay at Cirencester he conducted a considerable amount of research work for Professor A. H. Church in animal and vegetable chemistry, on turacin, a bird pigment from the Turaco, containing copper; colein, the colouring matter of the Coleus plant; vegetable albinism; aluminium in plants; eugenol; etc. Being registered as a teacher by the Science and Art Department, South Kensington, he gave a course of lectures at Cirencester in 1874 on inorganic chemistry. In 1878 he was elected a Fellow of the Institute of Chemistry. From 1878 to 1886, Woodcock was associated with the late G. W. Wigner and Messrs. Wigner and Harland, in their practice as analytical and consulting chemists and public analysts.

In 1886 he received an appointment with the American and Continental Sanitas Co., and accompanied the writer to New York, U.S.A., in order to start a factory and branch business in that country, remaining there until March, 1906, when he returned to England and joined the parent Sanitas Co., Ltd., in order to assist the writer in his charge of the chemical and bacteriological laboratories of the company, of which Mr. Woodcock subsequently became a director. During his stay in New York he was largely instrumental in initiating the New York section of the Society of Chemical Industry, and served as honorary treasurer from its formation, a farewell dinner being given to him by the members on March 24th, 1906. He also served as a Vice-President of the Chemists' Club, New York City. Ill-health caused him to resign active work with the "Sanitas" Co., Ltd., in March, 1916, but he remained on the board of directors up to the time of his death.

The research work in which he was engaged with the writer during this latter period of his career was very varied in character, and embraced the results covered by the following joint publications: "Bacteriological Testings of Certain Disinfectants, and the results as Affected by Varying Conditions." (Communicated to the British Pharmaceutical Conference, Cambridge, 1910. *Pharm. J.* 1910, **85**, 157). "The Bacterial Testings of Disinfectants. A Practical Criticism." (*Analyst*, May, 1913.) "The Production of

Formic Acid by the Atmospheric Oxidation of Turpentine." (*J. Soc. Chem. Ind.*, 1910, **29**, 791.) "The Production of Formic and Acetic Acids by the Atmospheric Oxidation of Turpentine." (*J. Soc. Chem. Ind.*, 1912, **31**, 265). "Some Experiments concerning Antiseptic Inhalations" (*J. Clinical Res.*, 1914, October.)

Mr. Woodcock was a member of the Society of Public Analysts, an original member of the Society of Chemical Industry, and served as a vice-president of that body for some years.

The writer first made the acquaintance of his late lamented friend in the rooms of the Chemical Society in the spring of 1872, and enjoyed unbroken friendship down to the time of his decease. Mr. Woodcock, if not a rapid worker in the laboratory, was most exact and painstaking—almost to a degree of fastidiousness—so that his work was always eminently trustworthy. He was of genial character, extremely well read, of the highest rectitude, and his loss will be deeply mourned by all who knew him at all intimately.

C. T. Kingzett.

PHILIP JOHN WORSLEY.

Born October 29th, 1834; Died March 7th, 1917.

Philip John, the son of Philip Worsley, was born in London and lived there during his school and college days. His taste for chemistry showed itself when he was quite young, and was encouraged by his grandfather, John Taylor, F.R.S., and his uncles, who were mining engineers. He entered the Junior School of University College, Gower Street, in September, 1843. In speaking of his school days, he said that he was not successful because he seldom kept his mind continuously on his work; classics did not come easily to him, and he had the greatest difficulty in learning by heart, but he was interested in chemistry. However, he worked better when he went to University College in 1850, where he greatly appreciated the teaching of Augustus de Morgan in mathematics and of Thomas Graham in chemistry. He graduated in 1853 with honours in chemistry. Among his fellow-students were George du Maurier, Michael Foster, George Carey Foster, and George Buchanan. The great exhibition of 1851 brought many distinguished scientific foreigners to his grandfather's house in Kensington, which gave the young student of chemistry and prospective mining engineer opportunities of hearing discussion on all the latest discoveries and theories.

In 1853 he went with his uncle, Richard Taylor, on a visit to lead mines at Pontgibaud in the Auvergne, where he was given the run of the works. From Pontgibaud he went by coach to Marseilles, the railway not being opened beyond Lyons; here he

stayed with a great-uncle, Philip Taylor, who had engineering works, which have since become one of the shipbuilding yards of the French Navy—les Forges et Chantiers de la Méditerranée. His next experience was in Germany, where he went to be educated as a mining engineer at the Bergakademie, or Royal School of Mines, at Freiberg in Saxony. On the way he passed through Heidelberg, and was taken by his friend Henry, afterwards Sir Henry, Roscoe to see Bunsen's laboratory. Before attending lectures at the Bergakademie, the students had to take a practical course either in the mines or the smelting works; Worsley chose the latter. On his own initiative he made careful notes of the process accounts, giving the results and cost of the various operations, which were invaluable to him in later days. On his return from Germany in 1854 he took a course of practical chemistry in the Birkbeck Laboratory at University College, London, under Professor Alexander W. Williamson and Assistant Professor Henry Watts, author of the well-known "Dictionary of Chemistry."

In 1855 came his first employment. He was sent to Ireland to assist Dr. Gurlt, a former Freiberg student, in working a new process for extracting copper from poor ores for the Wicklow Copper Co. This only lasted for a month or two, his first regular work being at Rotherhithe, where he started works for Messrs. H. J. Enthoven and Sons for separating silver from lead, superintending the erection of the plant, and constructing subsidiary furnaces from his own plans. While here he joined the Chemical Society, being elected a Fellow on February 4th, 1858. He stayed at Rotherhithe until 1860, when he went to Bristol as assistant manager of the Netham Chemical Works.

In the autumn of 1856 his grandfather, who was treasurer and an original member of the British Association, took him to the meeting at Cheltenham and made him an associate. His friends of the Chemical Society put him upon the committee of Section B of the Chemical Section. It was at this meeting that Sir Henry Bessemer described his process of burning the carbon out of pig-iron, which was the first step towards the modern process of making Bessemer steel. In 1858 Philip J. Worsley and George Carey Foster went together to the meeting at Leeds, where they met the set of young chemists whom he had seen working in Bunsen's laboratory at Heidelberg in 1854. They did not appreciate the social evenings of the Association, but met in each other's rooms and formed what they called Sub-Section B; these meetings were full of fun and interest, and other friends besides the original members asked to be allowed to join them.

In 1860 the Chemical Works at Netham were a small affair with a capital of £15,000. They had been going for a year and a-half,

and were in a very bad way. The new young assistant manager was thrown entirely on his own resources; he knew the theory of the processes, but in practice all was new to him. He soon found that the business was not prospering, and that unless he could improve the manufacture it would soon come to an end. He gradually introduced improved methods and instituted a system of regular sampling and testing the various stages of the work. Common sense with theory as a guide soon began to tell, and the reign of chemical anarchy and muddle gave place to order and system. After three months of probation he was made manager. After a time Netham chemicals got a high repute and were in constantly increasing demand. The plant and capital were increased every few years, and the directors' appreciation of his management was shown by their giving him a place on the board in 1871.

In 1873 he joined with other alkali manufacturers to form the Bleach Association, at which he made the acquaintance of all the leading men of the trade, some of whom were already his friends or schoolfellows. At a later period, when the Netham Chemical Company was merged in the United Alkali Company (1890), he met many of them again and worked with them as a fellow-director, keeping his seat on the board until 1901.

As a young man, Worsley's strong inclination was towards pure science. He imagined that he would always be able to keep up his interest in chemistry, and that he might in his leisure find time to make investigations which would establish him as the equal of the men of science who were his friends. However, instead of working in a private laboratory, he gave his scanty leisure to the cause of education and philanthropy. From the chairmanship of the St. George's School Board (Netham is in the parish of St. George, Bristol) to the vice-chairmanship of the University College, afterwards the University of Bristol, he helped to forward every grade of education in the city. As a Liberal in politics and a Unitarian in religion, he took an active part in public life. His chief recreation in his later years was gardening, and one of his greatest pleasures was the success he obtained in producing new varieties of daffodils by hybridisation.

As a memorial of his great work in connexion with the University of Bristol and his interest in the chemical department, a gift has been made to the chemical library, the interest of which is to be used annually to make additions of books and periodicals. He had given the greater part of his private collection of books on chemistry to the University during his lifetime. A. W.

The Old and the New Mineralogy.

Hugo Müller Lecture, delivered before the Chemical Society on April 18th, 1918.

By Sir Henry Alexander Miers, F.R.S.

When I was honoured by the Council of the Chemical Society with the invitation to deliver the first Hugo Müller Lecture, I was in some doubt whether I ought to accept it. The task it involves is not easy for one who during the last ten years has by administrative duties been taken altogether away from scientific work and who has not been able even to keep in touch with the rapidly increasing literature either in chemistry or in mineralogy.

But when I thought of my old and close friendship with the man in whose memory this lecture has been instituted, and the regard which I feel for his family; when I reflected on the helpful part that he played in strengthening the bond of union between mineralogy and other sciences; and in particular when I remembered the kindly interest with which he encouraged me in my younger days, I felt that the invitation of the Council laid a duty on me which I could scarcely refuse, however ill-qualified I may be to fulfil it adequately.

The excellent obituary notice of Dr. Hugo Müller in the June (1917) number of the Society's Journal sketches in clear outline both the character and the scientific career of this singularly modest and wide-minded man. All who knew him will feel that in him they have lost not only a warm-hearted and sympathetic friend, but also an adviser whose sound judgment and varied knowledge were only equalled by the unselfishness with which he placed them at the disposal of others.

There can, I think, be no more kindly or more useful action than to help young people at the outset of their career to do the work for which they are best fitted by training and inclination; and I am able to speak as one who owed to him, at least to some extent, an introduction to congenial work.

As Professor Armstrong has recorded in the obituary notice to which I have referred, it was largely owing to Dr. Müller's instrumentality, when as President of this Society he was a member of the Executive Committee of the Central Technical College, that the teaching of crystallography was introduced into the Chemical Department of the College.

That was really the first recognition in this country of crystallography as an independent subject, and the first recognition of its

importance to chemical students. I only regret that the recognised position given to crystallography by Professor Armstrong's action has apparently been lost by his retirement.

I was invited by Professor Armstrong to undertake the work, and was thus given the opportunity of teaching a subject in the practice of which I was engaged by my daily occupation as assistant in the Mineral Department of the British Museum.

You will understand, then, that I am glad for this among other reasons to have this opportunity of offering a tribute to Dr. Müller's memory.

Hugo Müller's interest in minerals began in his boyhood, and was no doubt stimulated during his student days at Leipzig by the influence of Professor C. F. Naumann, whose lectures he attended. Indeed, Professor Armstrong tells us that his first intention was to devote himself to geology; and although in later life his professional energies became more and more absorbed by chemistry and its applications to the industry with which he was concerned, and his leisure hours by botany and gardening, yet he always maintained his interest in minerals and mineralogy, and his acquaintance with the literature of the subject. Indeed, from 1901 to 1904 he was President of the Mineralogical Society.

He was always a great admirer of fine mineral specimens, and left behind him a very complete and representative collection which has been presented by his widow and daughter to my old department in the University of Oxford.

It may seem singular that with so pronounced an affection for minerals Müller was much more concerned to devote his analytical skill to vegetable than to mineral products. When he retired from business he carried on researches into the chemical constitution of organic products, mostly of vegetable origin, and did not, as might have been expected, take up work on the minerals, in which he was so deeply interested. In fact, his published mineralogical work was actually confined to the early years between 1850 and 1860.

Whether he ever intended to do scientific work on his mineral collection I am unable to say; but had he done so on his retirement from business, it would have been in very different circumstances from those which prevailed fifty years earlier, especially as regards the attitude of mineralogists towards chemistry.

It has occurred to me that I may make the present occasion an opportunity for contrasting this attitude as it was in 1850 with what it was at the beginning of the twentieth century when Müller retired from business, and what it is at the present day.

The period of his student days in Leipzig seems to me to have been a very interesting and a very critical period in the history

of this science, which was then just beginning to recover from a dangerous disease.

To explain what I mean, let me recall the views which were held by many of the most influential mineralogists at, or shortly before, that date.

In the mineralogical world, full sway was then still exercised by the "natural (or natural history) system" of Werner, of Freiberg, which had been developed and elaborated by his successor Mohs.

According to this system, and here I am quoting the words of Mohs himself, "Mineralogy is the natural history of minerals," and "the natural-historical properties are those with which Nature has endowed the bodies which it produces, provided those properties as well as the bodies themselves remain unaltered during the examination." The only characters of minerals, according to this view, which are of fundamental importance, and which are therefore to be used for the purpose of discriminating between species and of classifying them, are the external or natural-history properties, such as specific gravity, lustre, hardness, colour, frangibility, and crystalline form. Clearly this definition entirely excludes the chemical properties. To quote again the actual words of Mohs: "Properties which can only be used during or after a change cannot be employed agreeably to the principles of Natural History and must therefore be excluded from mineralogy. Properties of this kind are the fusibility of minerals examined before the blowpipe; their solubility in acids; phosphorescence produced by heat; chemical analysis instituted to ascertain the quality or relative quantity of the component parts." "If a person intends to acquire solid information in mineralogy he should examine well-arranged collections."

These views served, no doubt, to stimulate collectors of minerals and directed a good deal of attention to the desirability of bringing together the best possible specimens, and of comparing the external characters so as to discover their relationships. But that the chemical properties should be completely ignored on principle seems now almost incredible, especially when we remember that Berzelius had already published in 1816 a chemical classification of minerals and had even claimed that mineralogy is really only a branch of chemistry. The authority of Berzelius was even greater than that of Werner or Mohs; yet their methods persisted for another generation at Freiburg, which, as a great mining centre, was also a great centre of instruction in mineralogy.

It was during Müller's student days that the revolt against their ideas took place.

To obtain a general survey of the successive changes in the history of the science, one cannot do better than refer to the successive editions of J. D. Dana's "System of Mineralogy," which first appeared in 1837, and of which the sixth edition (1892) was prepared by his son and successor, E. S. Dana. In the first and second editions Dana not only adopted the natural history system then in vogue, but even endeavoured to make it more precise by a Latin nomenclature; but in the third edition, published in 1850, he suddenly shook off the trammels of this system and adopted a chemical classification.

Nothing could better illustrate the change which came over the science in the middle of the nineteenth century than the preface to this edition. In it the author says: "The Science of Mineralogy has made rapid progress in the past six years; chemistry has opened to us a better knowledge of the nature and relation of compounds; and philosophy has thrown a new light upon the principles of classification. To change is always seeming fickleness. But not to change with the advance of Science is worse; it is persistence in error; and, therefore, notwithstanding the former adoption of what has been called the Natural History System, and the pledge to its support given by the author in supplying it with a Latin nomenclature, the whole system, its classes, orders, genera, and Latin names have been rejected. . . . The system has subserved its purpose in giving precision to the science and displaying many of the natural groupings which chemistry was slow to recognise. But there are errors in its very foundations which make it false to nature in its most essential points; and, in view of the character of these errors, we are willing it should be considered a relic of the past."

The year in which these words were written was the very year in which young Hugo Müller entered the University of Leipzig.

It must have required no small courage for a man in Dana's position to make such a recantation, but the benefit to the science was great. His "System" was becoming the standard book of reference for systematists. His rearrangement of species and adoption of a classification based on chemical constitution carried much weight.

It is not surprising that Hugo Müller as a student became interested in a science which was just at that time the focus of a discussion involving such fundamental issues, a science which in spite of its antiquity and importance had for thirty years, in Germany at least, endeavoured to close its doors against the chemist. It is fortunate that there were a few men like C. F. Rammelsberg and Gustav Rose who perceived the vital import-

ance of chemical composition in the study of minerals and exercised sufficient influence to counteract the dangerous authority of Mohs. Rammelsberg in 1847 published a volume of translations of the works of Berzelius bearing on the classification of minerals, and was devoting himself to their systematic analysis. I have already in a memorial lecture sufficiently described to this Society his contributions to the subject. It was his analytical work which really rendered possible a scientific classification. Gustav Rose in 1852 published his crystallo-chemical mineral system, which has served as the basis of all scientific classifications of minerals since that date. In the preface to that work he says: "It might appear that I have adopted a mixed principle in constructing this system: but this is not the case. For though I fully agree with the view of Berzelius that the system should only have regard to the nature of the elements combined, and the formulæ which express the composition, yet it must be borne in mind that the crystalline form is merely the expression of a definite composition, and in this way it is all the more certain a guide because in many, perhaps most, minerals we are still far from such a complete knowledge of the composition as is required by Nordenskiöld's system. The crystalline form tells us much more than the mere chemical formula; it tells us how the atoms are united, and this difference in the mode of union of the atoms often conditions the external differences of bodies even more than the actual differences between the atoms."

Dana, even when he originally adopted the natural system in preference to the chemical system, had expressed the hope that in time the two would prove to be identical: but the principle of isomorphism which was destined to effect this reconciliation seemed at that time to be only an obstacle.

For example, Whewell, in an essay on the classification of minerals, published in 1828, had pointed out how desirable it would be if some coincidence could be found in the chemical and mineralogical systems; but he argued that the then recently discovered property of isomorphism rendered a chemical classification impossible, since a mineral may be from the chemical point of view a mixture of an indefinite number of species.

In his "History of the Inductive Sciences," thirty years later, he still despairs of the attempts to reconcile the two systems, and says: "The combination of chemical, crystallographical, physical, and optical properties into some lofty generalisation is probably a triumph reserved for future and distant years."

The conflict between the two systems was to some extent prolonged by the fact that, even though the purely chemical system might be scientifically correct, it did not afford the means of prac-

tically distinguishing between mineral species except by long and elaborate analyses, and even these might fail, since different minerals may have what is apparently the same percentage composition; on the other hand, the external characters did enable the well-trained mineralogist to determine a species with rapidity and precision. It was perhaps natural, therefore, that Freiberg, the centre of training for miners and practical mineralogists, should espouse the system of Werner and Mohs.

Naumann, who had been professor at Freiberg before he came to Leipzig, may have been predisposed in favour of it, but he did himself adopt a system based on the chemical characters; for, as he said, "they represent the actual material, the substratum which is the basis of all morphological and physical phenomena, and which finds its scientific expression in the chemical formula." But he was even more of a crystallographer than a chemist, and emphasised the equal necessity of taking form as well as composition into account. His text-book, "Elements of Mineralogy," ran through five editions between 1846 and 1859, and exercised a far-reaching influence. In the later editions, his system was practically identical with that of Rose.

I have dwelt at some length on the controversy between the adherents of the two systems of classification, not only because it was a controversy which divided mineralogists into two schools of thought, even up to the time when Müller went to Leipzig, but also because a very important principle was at stake and because little is said about this in the histories of chemistry where the controversy is mentioned. It was not merely an academic question of classification or one of practical utility, neither was it a matter which only concerned mineralogists. It was really a question of mental attitude towards scientific problems.

At the beginning of the century there had been a somewhat similar struggle concerning the relative importance of chemistry and crystallography for mineralogists. This resulted from the great advances in crystallography made by the Abbé Haüy following on the great advances in chemistry made by Berzelius. But at that time there was no reaction of the sort represented later by Mohs and his school. Even Werner himself was not prejudiced like his successors. He attached the greatest importance to chemical composition in a system of classification, whatever exaggerated views he may have held concerning the value of external characters for the practical determination of mineral species.

The contrast between the attitude of Mohs and that of Haüy is evident to anyone who reads the introductions to their respective treatises on mineralogy.

In his zeal to confine the science within what he considered its proper bounds, Mohs endeavoured to dissociate it not only from chemistry, but from geology. "Natural History," he says, "considers the natural products as they are and not how they have been formed." And again: "It is a matter of the highest importance to keep the sciences perfectly distinct from each other and strictly within their respective limits."

Haüy, on the other hand, had recognised to the full the value of co-operation between all the sciences concerned, including not only chemistry, but also physics and geology.

The contention of Mohs and his school that it was unnecessary, or even improper, to apply chemistry to the study of minerals, seems to me to represent the most dangerous mental attitude which is possible for a scientific man.

We are apt to regret the growing specialisation in science, and to think that half a century ago it was almost impossible for a scientific worker to be much of a specialist. But surely the school of Mohs was guilty of the worst type of specialisation. The earlier workers in general were no narrow specialists, because the dividing lines between the sciencs were not decisively laid down. To Haüy, or Mitscherlich, to Wollaston, Brewster, or Rose, each discovery was a new scientific problem, and they were not much concerned to decide whether to use the methods of physics or chemistry or geology for its solution.

Frontiers have always been the scenes of greatest activity, and it is precisely on the borderland between two sciences that the most fruitful progress has been made.

A man is not a specialist to the detriment of himself or his science, even though he devotes his whole life to the study of a single problem, provided that he makes sufficient excursions over the frontier in the interests of his life's work. But Mohs and his school endeavoured to isolate mineralogy (including crystallography), and to make it an independent science apart from chemistry, physics, and geology, instead of regarding it as a meeting ground of these sciences. The aloofness engendered by their action did great harm both to mineralogy and to chemistry; it tended to withdraw mineralogy and crystallography from the purview of chemistry, and it also closed the eyes of mineralogists to advances in chemistry that should have been of vital importance to them.

History repeats itself, and what has happened before may happen again. This lectureship will, I hope, always be one of the safeguards against exclusiveness and specialisation and will aid mineralogists and chemists to understand and help each other. If

it does this, it will perpetuate the spirit of the man whose name it bears.

The harm of this isolation extends to matters that appear to concern only systematic mineralogy, such as classification. After all, a classification which is right or wrong for minerals must be also right or wrong for other crystallised substances if it is based on what is essential; its merits or shortcomings would sooner or later be disclosed if the underlying principles were applied to other substances.

One regrettable result of the policy of isolation was that for a long period the study of minerals was divorced from that of organic or even of other inorganic substances, and that the study of crystallography was confined to mineralogists. This was partly, no doubt, due to the fact that minerals afford such splendid examples of crystallisation, and partly because a knowledge of the crystal properties is so useful in their practical identification.

Let me here finish with this subject of classifications and remind you that it was not until a later period that attempts were made to include all crystallised substances in a wider scientific survey and in a common study. Indeed, it is only within the last few years that a comprehensive catalogue of them all has been attempted by Groth in his "Chemical Crystallography," which began to appear in 1896, and is not yet completed.

During the same period, the Russian crystallographer Fedorov has been constructing a general table of crystalline substances so arranged that it is possible to identify any known substance by means of the characteristic angle of a single crystal when once it has been set up in the right position according to the rules which he has formulated. Mr. Barker has recently shown in a striking example the practical utility of this table even for the purposes of the medical man, by thus identifying a minute crystal of salol of intestinal origin (*Lancet*, May 26th, 1917).

That there should be several classifications made for different purposes within the same science is probably a quite wholesome principle: one may, for example, bring out constitutional relationships, and another be useful for determinative purposes.

But of far greater scientific importance than the systematic classification of minerals or the discovery of new methods for their identification is the question, What are the actual relations between the physical, geometrical, and chemical characters of a crystallised mineral? Only in proportion as this study has grown by co-operation with chemistry and physics did the science of mineralogy advance successfully along the path opened up by Haüy and

Berzelius, by Mitscherlich and Wollaston, by Rose and Rammelsberg.

In this new purpose, and in the changed attitude of mind that it involved, lies, I think, the essential difference between the old and the new mineralogy which it is the object of this address to emphasise, and it is time for me to turn to the later developments.

The newer mineralogy with this purpose in view has only made progress by the employment of every available physical and chemical method in the accurate study of carefully selected specimens.

In the first instance, it was difficult to do much with isolated species for lack of suitable experimental methods, such as have been developed during the present century. Having ascertained the exact chemical constitution, to determine with any reasonable probability the actual arrangement of the atoms or molecules in a crystal which may account for its form and physical characters was too difficult a problem with the experimental resources then available.

But the relations between different minerals belonging to the same group in which it could be assumed that, whatever they may actually be, the structures and constitution are similar, were gradually worked out.

The laws of vicarious replacement of one element or radicle by another were studied, and the variations of physical characters with the change of chemical composition in many an isomorphous series constituting a mineral group were successfully traced; and it must be confessed that for these researches the foundations had not infrequently been laid by the adherents of the natural history methods, for they had recognised many minerals as belonging to very definite mineral species and groups in spite of their chemical differences.

It was understood, for instance, that the pyroxenes or the felspars, whatever might be their percentage composition, do constitute a group, and it was natural to conclude that the remarkable similarity in physical properties shown by the various members of the group must correspond to a mutual replacement of certain elements or radicles, though the exact nature of these radicles might be still doubtful. For example, the growing importance of petrography and the use of the polarising microscope led to a vast amount of study being devoted to such minerals as the felspars, so that it was not long before it became possible to determine with accuracy by means of the microscope the exact chemical constitution of a minute crystal grain belonging to this group without analysis.

On the other hand, it is still doubtful how the elements are actually associated with each other in the mineral, or what radicles are to be regarded as corresponding with each other in such isomorphous groups, mixtures, or solid solutions. To establish this sort of knowledge, a great deal of very careful chemical analysis was necessary, accompanied by an equally careful physical study of the specimens analysed. It was to work of this character that most of the important advances in chemical mineralogy during the second half of the nineteenth century are due.

I select as a conspicuous example of this type of research Penfield's investigation of topaz, to which a very definite chemical formula had been assigned, although it was known that the mineral exhibits some variations both in composition and in physical characters.

The most reasonable view seemed to be that the radicle AlO may be replaceable by the radicle AlF_2. The insignificant and variable traces of water were ignored. Careful analyses and accurate measurement of the angle between the optic axes, however, led Penfield to the conclusion that the optical characters vary regularly with the proportion of water, or rather of hydroxyl, and that the simple formula $Al_2F_2SiO_4$ is entirely satisfactory if it be understood that fluorine is replaceable by hydroxyl.

Many minerals and mineral groups have now been investigated with equal success: but almost every mineral contains an intermixture of various allied compounds as well as enclosures of other minerals, and therefore it is rather to the study of pure laboratory products that we have to look in the first instance for more precise knowledge concerning the relations between form, physical properties, and composition.

A vast number of isomorphous groups have now been studied in detail and with accuracy.

Tutton's classic investigation of the sulphates and selenates of potassium, rubidium, cæsium, and ammonium is one of the most conspicuous and complete examples. Others extending over the whole field of inorganic and organic compounds are recorded and discussed in Groth's "Chemical Crystallography."

I need only mention such studies as those of Jaeger on the benzene derivatives and the nitroanilines, of le Bel and Ries on the platinichlorides, of Jee, Rodd, Colegate, and others working with Armstrong on the benzene derivatives, and the investigations associated with the names of Gossner, Steinmetz, and others working with Groth at Munich.

All these advances in chemical crystallography have only been rendered possible by a vast amount of research on countless sub-

stances examined in the laboratory by a new generation of chemists who had acquired a knowledge of the methods of crystallography and an interest in its principles.

Although in these and similar investigations the exact morphological effects of the replacement of one element or radicle by another have been determined, I fear it cannot be claimed that the general laws of morphotropic action have been discovered even at the present day.

Now let me return for a moment to the year 1850. That year which, as I have indicated, was notable in the history of systematic mineralogy, was even more important in the history of crystallography, for it witnessed the publication of Bravais's memoir on the regular arrangement of points. This research first established a principle capable of explaining the homogeneity of crystals, their symmetry, the distribution of their faces, and their cleavage.

The mathematical treatment founded by him was elaborated by Sohncke and others, until finally and independently, towards the close of the nineteenth century, Schönflies, Fedorov, and Barlow determined and tabulated all the possible arrangements of material which can build up a homogeneous crystal, and so completed the pure geometry of the subject.

But when it came to the application of these geometrical principles to actual crystals and to the question what are the units which are arranged in this manner, it was the custom to fall back upon the assumption that these are "physical molecules" consisting of an unknown aggregate of "chemical molecules." Indeed, an attempt made by Sterry Hunt in 1891 to determine the degree of polymerisation from the specific gravity, hardness, and solubility led him to the conclusion that there are 584 chemical molecules in the physical molecule of calcite and 950 in that of quartz.

When speculation runs riot, it is a sign that experiment is needed. It is clear that there was need of new experimental methods to curb such wild views, and not only in this, but in other branches of mineralogy; for there were equally uncontrolled speculations concerning the origin of minerals, and especially rocks, and the processes by which they have solidified from solution or fusion.

It is in these later experimental methods that what I venture to call the new mineralogy distinguishes itself from the old mineralogy belonging to Müller's student days. And the change has mainly been rendered possible by recent advances in physics and chemistry, and particularly in physical chemistry.

There are two stages in the history of a crystallised mineral, that which terminates immediately before it solidifies and that

which begins at the moment of solidification. Both are of equal importance and interest to the mineralogist, and upon both a flood of new light has been thrown by recent investigation.

The excellent abstracts of the *Journal* of this Society and its "Annual Reports on the Progress of Chemistry" record all the important researches bearing on these problems. I need not do more, therefore, than select one or two conspicuous examples.

To deal first with the origin of minerals and the stages that preceded their crystallisation.

The application of the laws of physical chemistry, especially the recently discovered properties of solutions, found its most fruitful results in the studies of the Stassfurt deposits by van't Hoff and his pupils. There can be little doubt that we have now a well-established history of the manner in which these deposits have been laid down from solution and the nature of the solutions from which they have crystallised. Before these researches, there had been much speculation as to how such deposits might have originated from the evaporation of saline water, but it was only by the laboratory experiments begun by van't Hoff in 1897 and carried on through a series of years that the geological history of the deposits has been finally and fully reconstructed, including the order and conditions of deposit of more than thirty mineral species.

Nothing like this had previously been achieved. The processes previously invoked in explanation of the origin of minerals had been largely hypothetical, not experimental; with these researches, a new chapter in the history of mineralogy was opened.

It is unnecessary to refer to any details of the experiments. The excellent summary published by Dr. E. F. Armstrong in the British Association Report for 1901, and since that date the Annual Reports of this Society, have helped to make them widely known.

To take another example. It is of vital importance to the geologist that the history of rock formation should be deciphered, and for this purpose the newly established laws of physical chemistry were also directed to the problem of the crystallisation of the silicates.

Igneous rocks were for the first time regarded as solutions, and the physical properties of solutions were applied to the crystallisation of rocks from molten magmas. Vogt, in particular, endeavoured to show by his researches on slags, and with remarkable success, that they have crystallised in accordance with the laws of eutectic mixtures and of mixed crystals. A whole new field of research was thus opened up; but here again much of it was highly speculative until within the last few years the actual crystallisation of molten silicates has been brought within the range

of experimental study. Doelter, of Graz, and his pupils are responsible for much of this work, but more recently the experiments conducted at the Geophysical Laboratory at Washington have constituted a very remarkable advance.

The appeal to experiment has replaced a mass of speculations concerning theoretical solvents and the order of crystallisation, which were based only on field observations and bulk analyses. Now that sufficiently high temperatures can be attained, these investigations are of the greatest importance both to the geologist and to the mineralogist, since they reproduce in all probability the main conditions under which rocks have crystallised. One feels that for the first time the laws of their solidification are being traced and that they can be verified by experiment.

I need not do more than quote as examples the very full researches by Bowen and Anderson on the binary system magnesia and silica, and the ternary systems diopside–forsterite–silica and anorthite–forsterite–silica, and more recently by Bowen's investigations on diopside–albite–anorthite, and those by Rankine and Wright on the system lime–alumina–silica.

Such questions as the order of crystallisation and the actual position of eutectic mixtures in the process of solidification can now be determined by actual experiment, and not merely by the microscopical study of the solid rock. Not the least remarkable result of many of these experiments is the absence of the eutectic structure so characteristic of alloys, suggesting that perhaps too much importance may have been attributed to it by petrologists.

Some of this work has also thrown valuable light on the past history of rocks and minerals.

To quote only one example; direct experiments on the melting and inversion temperature of quartz have indicated that at 575°, within a very close approximation, it suffers enantiotropic change to the phase now recognised as β-quartz, and that above 800° quartz is no longer stable at ordinary temperatures, but becomes converted into tridymite. It is therefore suggested that quartz may be used as a geological thermometer serving to record the maximum temperature which has been reached by certain rocks. A similar use may perhaps be made of other minerals.

Such work as that of Bowen on the melting points of the felspars and their mixtures is of the highest value in tracing the past history of rocks and their minerals. His conclusion that albite and anorthite have the same molecular complexity in the liquid as in the solid state is one more stage in the simplification of our ideas concerning the constitution of minerals.

The pressure is, of course, an all-important factor which must

not be left out of account in speculations concerning the past history of rocks. Change of pressure may affect the order of crystallisation of the minerals which separate, and may determine their nature, as profoundly as change of temperature. Experiments at high temperatures combined with high pressure are now for the first time becoming possible with improved laboratory apparatus.

These experimental researches on the application of the law of solutions to minerals are not confined to silica and the silicates, but have already been extended at the geophysical laboratory to the copper sulphides and the oxides of iron. Experiment has yet to be applied successfully to such questions as magmatic differentiation, the effect of mineralising agents, pneumatolysis, and many similar problems. On the more vexed questions relating to the history of vein minerals and the large class of secondary deposits which line the cavities and fissures of the earth's crust, experiment will have much to say, though it may be a long time before experimental investigation on these subjects can be fully developed.

In the work of van't Hoff and in that of the Washington geophysicists, we have two conspicuous examples of what I mean by the new mineralogy as applied to the problem of the origin of minerals and rocks, that is, to the stage through which they pass up to the moment of solidification.

This application of experimental methods in which an attempt is made to realise the conditions of mineral growth replaces a vast amount of speculation with which the science was burdened during the last fifty years, and it unsettles some of the elaborate classifications, especially of rocks, which have occupied too much time and thought during the same period.

Surely classification as a means of arriving at general laws is an unsafe guide in the inorganic world if based to any large extent on hypotheses; it only serves to perpetuate them. Its proper function is to record the application of the general laws established by experiment, and any classification must inevitably change with new experimental results. For this reason, the attempts which are now being made by a group of American geologists to establish a natural classification of rocks with a new nomenclature are surely doomed to share the fate which befell the natural classification of minerals.

Let us turn next to those problems that concern the nature of minerals after they have solidified.

In this field also there had been an immense amount of speculation during the last half of the nineteenth century concerning the nature and arrangement of the units which constitute a crystal,

Somewhat surer ground was reached by the conception of topic axes introduced by Becke, and employed by Muthmann and Tutton, which gave suggestive evidence concerning the relative dispositions of the crystalline units along corresponding directions in a series of isomorphous substances, and indicated the increased or diminished separation of these units along a given direction when one element or radicle is replaced by another.

The importance of the molecular volume in these relations has been emphasised by Barker's experiments on the parallel growth of one substance on another; I have considerable faith in this as a sure experimental method which has yet to be used in tracing similarities of structure even where there is no chemical relationship.

The crystallographic study of closely allied substances has further led directly to speculations concerning the relative positions of the *atoms* in the crystal structure, as, for example, in Muthmann's study of the perchlorates and permanganates, which was the first conducted from the point of view of topic axes; and, again, the relationships between the nitrates and carbonates led early to similar speculations concerning sodium nitrate and calcite.

To take another example in which this problem was attacked in a different way, Sollas endeavoured to ascertain the positions of the elements in sodium nitrate by comparing the specific refractive energy of the crystal in its two principal directions, and in the case of potassium copper chloride he combined this feature with the dichroism which he interpreted as indicating that the crystal is of a cuprous nature in one direction and of a cupric nature in another.

It is interesting to note that such speculations were already assuming that in most crystals the structural unit is probably an aggregate of not more than a few molecules, and in some perhaps the molecule itself. This was a great contrast to the earlier assumptions concerning polymerisation in the crystal molecule. Indeed, it was not long before expression was given to the extreme view that the structure is to be regarded as a regular arrangement of atoms in which the grouping into molecules is merely a geometrical fiction, whatever may have been their significance immediately before the act of crystallisation. This view was stated in a paper read by Professor Groth to the British Association as far back as 1904, in which, speaking of new ideas concerning crystal structure, he said, "it is unnecessary to assume the operation of any 'molecular forces' in addition to the forces which act upon the atoms themselves."

If, as I have said before, we are not yet in sight of the general

laws of morphotropic action even within groups of closely allied substances, we are still further from the supreme problem how from the chemical composition of a substance to deduce the form and physical properties of its crystal. The great test of a theory is the question whether it will enable us to predict, and in this sense there is as yet no satisfactory theory of the nature of a crystal. A bold and original attempt has been made by Pope and Barlow with some measure of success, and their theory of crystal structure which is based on the atom as the structural unit and endeavours to explain the form of the crystal from the atomic magnitudes, as indicated by the valencies, combined with the principle of close packing, has already inspired several very important investigations.

But in regard to the structure of the solid crystal, just as much as for the process of crystallisation to which I have already alluded, the need was for new experimental evidence—for some method of investigation which could explore the structure with a finer discrimination than that provided by the transmission of light or heat.

And now, as all the world knows, it seems that direct evidence concerning the arrangement of the parts of a crystal, the magnitude of the intervals between them, and even the spacing of the atoms, is supplied by X-ray methods, and in particular by the classic investigations of the Braggs.

In the history of crystallographic discoveries it has not infrequently happened that the crystal has first revealed some unknown physical phenomenon, has then supplied the mechanism or the material for studying it, and for establishing the principles by which it is governed; then, finally, these principles have been turned back upon the crystal in order to explain its nature. This was so with the phenomena of double refraction; calcite disclosed the new fact of double refraction to Bartholinus and Huygens, and this led to the discovery of the laws of propagation of light; these in turn were applied to the study of crystals, and have proved the most potent instrument that we possessed until lately for researches into crystalline structure. It was so again with circular polarisation and with pyroelectricity.

And so it is now with the new X-ray methods. The crystal reveals the new facts and then lays itself bare to attack from the physical weapon which it has forged. Indeed, in these remarkable investigations it is difficult to say which is the more valuable, the evidence which the crystal gives concerning the nature of the radiations or the evidence which the radiations give concerning the molecular or atomic intervals in the structure of the crystal.

If I do not dwell at length on these researches, it is not through any failure to recognise them as by far the most important advance of recent years, even in the science of mineralogy, but only because they are now so familiar to the scientific world. They have, of course, not destroyed anything that had been established by mathematical deduction from previous experimental evidence, but they have supplied new experimental methods of a most fundamental character for the study of crystals.

The assumption on which Bragg's interpretation is based, namely, that the crystal consists of material distributed in equally spaced plane layers or in layers separated by intervals which recur regularly, corresponds with all that had been laid down by purely geometrical considerations, and it has been confirmed by all that we know about the physical properties of crystals.

Indeed, if it were needed, evidence of the existence of plane internal layers parallel to possible faces of the crystal is supplied by the *X*-ray analysis. For Canac and others have shown that it is possible to measure the angles of a crystal by *X*-ray reflections from the internal planes just as certainly and almost as accurately as by the reflection of light from the external faces of the crystal.

The care which must be exercised in the interpretation of *X*-ray measurements in their present early development is illustrated by Vegard's observations on the rutile group of minerals, in which a structure based on the reflections observed by him has been subsequently shown to be erroneous, because certain intermediate reflections were overlooked.

Whether the *X*-ray analysis can supply evidence as to the existence or nature of the chemical molecule in the crystal is a more difficult question into which I do not feel competent to enter.

In crystallographic research I have nothing to record quite corresponding with the work of the Washington geophysicists, for the simple reason that there is for crystallography no department corresponding with the geophysical laboratory.

In my opinion, the importance of the study of crystals has now become so great, not only for the identification of substances by crystal measurement, but also on account of the new knowledge which modern crystal study is contributing to problems belonging to different sciences, that there is real need for a department of pure crystallographic research, one in which such studies can be carried out quite independently of elementary teaching or of immediate applications, and without being tied to mineralogy. I venture to hope that it will not be long before some such department is founded either in connexion with one of our universities or elsewhere.

There is yet another notable field of work in which the later physical discoveries have opened up new experimental methods in mineralogy. The past history of minerals may now be discussed in the light of their radioactivity, and the study of radioactive changes is giving some indication of a process of progressive change, if not in the minerals themselves at least in the elements which they contain. For the first time, therefore, speculations concerning the age of certain minerals can be based on direct experimental evidence.

The remarkable pleochroic haloes which surround zircon and other radioactive minerals enclosed as microscopic crystals in mica, cordierite, and other rock-forming minerals, were investigated by Joly from this point of view; and in the hands of Strutt, Boltwood, and others the proportions of uranium, radium, thorium, helium, and lead in radioactive minerals have been made an instrument not only for exploring the history of the disintegration changes in these elements, but for estimating the actual age of the minerals. A new importance now attaches to the accurate analysis of such minerals in respect of rare elements which previously escaped notice, and also to the choice of the specimens analysed, for, as Boltwood points out, it is necessary to distinguish between the more ancient primary minerals and those of secondary, and therefore of more recent, origin.

From the mineralogist's point of view, we have passed out of the stage in which the object is to ascertain the formula and to study the mutual replacements of elements and radicles in order to classify minerals into definite species, and have begun to study the mode of association of the elements and radicles within the mineral, both now and during its past history.

In selecting only three or four conspicuous examples of the progress of mineral chemistry during the last fifty years, I have, of course, passed by without notice many very remarkable advances made in other branches of the subject, such as analytical methods and interpretation of analyses, the synthesis of individual minerals, the alterations, replacements, and transformation of minerals both in nature and in the laboratory, the improvements in apparatus for the accurate measurement of physical constants, new methods of separation, the introduction of microchemical analysis, the relations between colour and radioactivity, and a host of other advances.

I have also omitted specific mention of all the recent work on the constitution of the natural silicates, and this for a reason which I must state.

The history of modern views concerning this, the most important

group of minerals (constituting with silica about 90 per cent. of the earth's crust), begins, not long after the period to which I have confined my survey, in 1864 with Tschermak's discovery of the nature of the felspar group as mixtures of albite and anorthite. This led the way to attempts to explain the analyses of many other complicated silicates as mixtures of compounds not so similar to one another as those which had previously been classed as isomorphous, and in some instances far more dissimilar than albite and anorthite.

When, however, such minerals as the pyroxenes, amphiboles, mica, and tourmaline were discussed, the analyses could only be interpreted on this principle by the aid of a host of possible silicates which are not known to exist; and although some experimental guidance in these speculations has been supplied by the work of Tschermak, Schneider, Thugutt, and others on the acids which could be isolated or the residues which could be obtained by decomposition of the mineral, yet the interpretation of the analyses remained to a large extent hypothetical.

The evidence supplied by pseudomorphs, which show the initial and final products in the case of an altered mineral, cannot give any sure information about the solvents which have acted or the intermediate minerals which may have been produced during the process of change. Even experiments on the decomposition of silicates only in general produce compounds which are stable, and lose sight of compounds, unstable in themselves, which may enter into the constitution of the mineral. In the pyroxene group, for instance, synthetical experiments indicate that the diopside molecule may form a solid solution with several unstable silicates, as well as with alumina or ferric oxide, so that Rammelsberg's view of the group as a mixture of the diopside molecule with alumina is not necessarily more unreasonable than Tschermak's more usually accepted interpretation founded on the analogy of the felspars.

And if we make a general survey of the views which have been expressed on the constitution of the silicates, and especially of the alumosilicates, including Vernadsky's theory of the chlorite nucleus and the mica nucleus, and the more recent and attractive hexite-pentite theory of W. and D. Asch, we have to confess that we are still waiting for more experimental evidence before we can be on sure ground. In so far as these theories suggest new experiments, they perform a most valuable function, but they are not to be regarded as in any way equivalent to experimental results.

Synthetical work such as that of Clarke, Lemberg, and Doelter; the discrimination of solid solutions from double salts by careful melting-point determinations; study of the properties of pure

artificial silicates, their combinations and disintegrations; the manufacture of additive compounds and derivatives; the study of such replacements as those of water by alcohol, benzene, and other substances in the zeolites investigated by Friedel, and the adsorption experiments of Grandjean—these are examples of the sort of researches which must be largely extended before constitutional or structural formulæ can be assigned with any confidence to the silicates, and especially to the alumosilicates.

For the present, the freedom of speculation which is possible concerning the chemical structure of minerals bears some resemblance to the unchecked freedom with which the physical and geometrical structures were handled before the advent of *X*-ray methods and the unrestrained speculations on the crystallisation of magmas and mineral solutions which prevailed before the experimental methods of physical chemistry were applied. We still await the key of experiment which may unlock the secret of the chemical constitution of the silicon compounds.

For this reason, without desiring to ignore their interest and importance, I pass over the whole subject of modern theories concerning the chemical structure of the silicates.

Let me, finally, ask the question: In what fundamental respects does the new mineralogy differ from the old of fifty years ago, and what are the prospects for the future? Is it anything more than the pursuit by new methods of the old problems? A more refined study than was possible then of the characters and properties of minerals? And the answer, I think, is that it is a great deal more than this, for the whole purpose of the quest has changed. Our object is no longer merely to trace the relations between different minerals, neither is it our purpose to classify them as animals and plants are classified in order to ascertain the laws that govern these relations. The importance of such classification and study of characters in the biological sciences is due to the fact that the record is one of constant change and development: the careful definition and study of species leads to the laws of evolution. In the mineral kingdom there is apparently no such prospect. Our main purpose is now not to discover how one mineral has been evolved from another, for there is no such evolution, or even how it is related to others, but how it has been constructed from its constituents. We are concerned with the question how its elements came together, and how they are united to form the mineral; and why among the elements that build up the earth's crust only certain combinations occur as minerals, whereas millions of combinations are theoretically possible. The wonder is not that there are so many minerals, but that there are so few; that mineral

species, for example, are so vastly outnumbered by the species of insects.

So long as the crystal unit was supposed to be an unknown multiple of the chemical molecule, these problems seemed far from solution, but now that we appear to be better justified in dealing, not so much with the arrangement of molecules as with the arrangement of atoms in the crystalline structure, one cannot help feeling that the structure must be one of greater simplicity than the complicated silicate formulæ seem to indicate. We may surely hope that minerals will prove to be comparatively simple groupings of the elements, that the discovery of the laws which determine the limited number of minerals existing as stable substances will lead us to a clarified vision of the conditions which determine equilibrium in non-living matter on the earth's surface, and that we may expect an answer to the question why the elements have come together and how they are united to form the beautiful compounds which constitute the mineral kingdom.

This change in the scientific prospects of mineralogy is due to the advent of new experimental methods and principles. The promise of a revived interest and an increased progress in this science lies in the application to minerals of every new experimental treatment, physical or chemical, that can be employed.

In this, as in many other sciences, far too much energy has been expended in the past on the repetition and refinement of old investigations, on the mere improvement of old methods of research or of apparatus, on questions of nomenclature or description. Although I do not wish to underestimate the value of accurate data patiently accumulated by prolonged and careful research, without which no sound foundations can be laid, yet I feel that for long periods mineralogy stagnated because time and energy were occupied in compiling interminable lists of uncertain crystal faces or in the analysis of impure specimens.

The real advance takes place when new methods of attack are turned upon the old subjects.

The physical properties of solutions, *X*-ray analysis, and radioactive changes are the three examples which I have quoted; they have infused new life into the science; but they are only three, and will have to be multiplied indefinitely.

Minerals deserve all the study that they can get; they supply the most perfect and the most varied materials; almost every known element is contained in them; they are extraordinarily stable compounds; they teem with problems, owing to the variety of conditions under which they exist or have been formed.

Especially would I attach importance to the fact, too often for-

gotten, that mineralogy is one of the natural history sciences, and therefore deals with natural objects not only as we find them in museums, but investigates their relations and their past history; while it studies their properties by applying to them all the known resources of the laboratory, it also studies through them the operation of the laws of nature, both now and in the distant ages of the past. In mineralogy, as in botany and zoology, it is in general impossible to reproduce past conditions; they have gone for ever. But there is this great difference between mineralogy and the biological sciences. Whilst they trace the history of changing species in the light of modern experiments and observations, the only record of their past, and that a secondary and an imperfect one, is supplied by fossils: the organisms themselves have disappeared.

On the other hand, in the case of crystallised minerals, we generally have the actual object surviving through the ages. The liquid carbon dioxide imprisoned in a quartz crystal, or the tiny zircon surrounded by its halo in mica, have been there for untold centuries and survive to tell the tale of their own history. The same is true of the radioactive mineral, which by its present composition gives a clue to past changes; the structure of the crystal remains as a permanent record of its original nature. We have in our hands the very object that existed millions of years ago, and not merely a cast of it, and we can continue on it the processes that nature has begun. The forces of crystallisation that brought together its component elements have held them together in the same relative positions, of which the unchanged form is the guarantee.

This circumstance gives a peculiar interest to the study of minerals; it is one which impresses a feeling of awe and fascination akin to that aroused by an ancient manuscript or a work of art which survives as a permanent record of the artistic life and thought of bygone ages, and, further, it invests them with a unique value for the decipherment of the past.

There is one other aspect of mineralogy which I wish to emphasise. I have directed attention to the fatal sort of specialisation and exclusion to which the natural history school of thought tended; but let me repeat that mineralogy is, nevertheless, a branch of natural history, and that the proper study of minerals, as of all natural objects, is in itself a safeguard against specialisation.

The true mineralogist must bring to this pursuit the resources of all the sciences; one who is merely concerned with the physics or chemistry or crystallography of minerals makes only a one-sided study of the subject. The more intense and concentrated the work of the true mineralogist, the less confined will it be: in fact, the

more he specialises in mineralogy, the less of a specialist does he become.

For this reason, the natural history subjects have a very particular educational value; they deserve to hold their own for educational purposes, and not to be broken up into specialised sections. They have a particular value, not only as a stimulating introduction to chemistry or physics or biology as taught in schools to beginners, but also as a means of maintaining interest in those sciences at a later stage.

In young children, the instinct for collecting is strong, and equally strong is the desire to know something about what they collect; by many of them, the approach to science is most easily made through an interest in natural history.

At the later stage, many older boys and girls on the literary side in the upper forms of schools, whose main interest is outside science and who realise that it will not play a large part in their lives, boys and girls to whom prolonged teaching of chemistry, physics, and biology (especially if they are separated by water-tight compartments) will be uninteresting, and therefore largely unprofitable might be made to retain their hold on the principles of all these fundamental sciences through the study of natural history.

We shall surely do well to utilise any interest that brings home to ordinary students the knowledge and conviction that science is not merely laboratory work, but that its principles are to be found in operation everywhere, though they may have to be explored in the laboratory. Those who specialise in language or history or literature must acquire this conviction by experience, just as those who specialise in science must learn by experience that all great literature is the expression of ideas, and that even scientific ideas cannot be expressed by an illiterate use of language.

A judicious employment of natural history will, I believe, do much to establish science in the place that it should occupy in our educational system.

When I accepted the invitation of the Council to deliver this lecture, I welcomed the opportunity it would give me of recalling to the Chemical Society this aspect of my favourite pursuit.

And, let me add, even for scientific workers in their later years a taste for natural history in any of its branches is worth maintaining as a very real corrective to narrow specialisation.

If an illustration be required, I cannot do better than remind you again of the wide scientific interests and achievements of the remarkable man whose name this lecture bears.

Mineralogy and botany appealed to his wide and catholic taste;

his love for minerals and plants was an abiding possession to him, not only because he loved them as beautiful things, but because he was a man deeply interested in natural objects and in the secrets of science that are revealed by them.

To those whose work lies in laboratories, such intercourse with nature is easily maintained, for there are many pathways that lead from experimental science to natural history.

Like Antaeus, they can always strengthen themselves by contact with Mother Earth, feeling with Wordsworth:

> "that Nature never did betray
> The heart that loved her; 'tis her privilege
> Though all the years of this our life to lead
> From joy to joy."

XXXII.—*The Synthesis of Ammonia at High Temperatures. Part II.*

By Edward Bradford Maxted.

In a recent paper (this vol., p. 168), the equilibrium between nitrogen, hydrogen, and ammonia at high temperatures was discussed from a thermodynamical point of view, and evidence was brought forward showing that in all probability the ammonia content of such a gas mixture in equilibrium, after decreasing with increasing temperature, eventually passes through a minimum and finally rises once more. On the basis of this theoretical indication of the possibility of a thermal synthesis of ammonia, it was shown experimentally that considerable yields of ammonia may be obtained by cooling a mixture of nitrogen and hydrogen extremely rapidly from the temperature of the oxy-hydrogen flame to that of the room.

In continuation of the above work, and especially in view of the known fact that a mixture of nitrogen and hydrogen may be completely converted into ammonia by sparking in a eudiometer over dilute acid (Donkin, *Proc. Roy. Soc.*, 1873, **21**, 281), an investigation was begun of the yields of ammonia obtainable from a rapidly cooled, high-tension arc, also by sparking, the present paper being a summary of the results obtained by induction discharge modified in such a way as to constitute a small, high-tension arc burning within a capillary tube, through which the mixture of nitrogen and hydrogen was passed.

By confining the action to a capillary tube, in the manner

described, the gas to be treated may be brought uniformly into contact with the discharge, and it was found easily possible to obtain at atmospheric pressure yields of ammonia amounting to 1·5 per cent. by volume of the gas-mixture taken for treatment. Induction sparks, as such, were found to exert a comparatively feeble action on the synthesis, energetic formation of ammonia only taking place when the electrodes were brought sufficiently close together to transform the ordinary spark discharge into a small, high-tension arc, accompanied by a visible and apparently continuous flame of high temperature.

EXPERIMENTAL.

The apparatus employed for the series of experiments about to be described consisted of a capillary glass tube having an internal diameter of 0·65 mm., an external diameter of 5 mm., and a length of about 10 cm. Platinum wire electrodes, 0·25 mm. thick, were sealed into the capillary tube in such a way as to leave a spark-gap of the size required, whilst the passage of gas through the tube was effected by means of fused-on glass side-tubes.

It was found inadvisable, on account of frequent fractures, to employ a heavy discharge, the most satisfactory conditions for the investigation being obtained with a "two-inch" coil, supplied with a primary current of from 3 to 3·5 amperes from the laboratory 220-volt main. Pure hydrogen and nitrogen for the synthesis were mixed in the proportion of three to one in a large gasholder and compressed into a cylinder for convenience in use. This mixed gas was passed at carefully determined rates through the capillary spark-gap, the ammonia formed being absorbed in dilute acid and estimated by means of Nessler's solution.

The first point to be investigated was the influence of the size of the spark-gap on the yield of ammonia, this gap being varied from 10 to 0·5 mm. while the rate of passage of the gas was first kept constant at 40 c.c. per hour, and, secondly, varied in such a way that the time of contact was kept at 0·0015 second for spark-gaps of various sizes. Table I summarises the results obtained by the first of these two methods, namely, with a constant rate of flow, table II those obtained by the second, that is, with a constant time of contact with the spark-gap, the primary current being in every case 3·5 amperes at 220 volts.

TABLE I.

Rate of Flow of Hydrogen–Nitrogen Mixture 40 c.c. *per hour.*

Length of spark-gap in mm.	Nature of discharge.	Percentage of ammonia by volume in issuing gases.
10	Spark	0·1
5	Incipient flame	0·25
1·5	Arc flame	0·8
0·5	Arc flame	1·1

TABLE II.

Estimated Time of Contact, 0·0015 *sec.*

Length of spark-gap in mm.	Nature of discharge.	Percentage of ammonia by volume in issuing gases.
10	Spark	less than 0·01
5	Incipient flame	0·04
1·5	Arc flame	0·5
0·5	Arc flame	1·1

It will be seen that as the size of the spark-gap is decreased, the flame loses its well-defined spark-like character and becomes a small but intensely hot high-tension arc, this flame, probably by virtue of its high temperature combined with the rapid cooling effect afforded by the relatively cold walls of the glass capillary tube, possessing the power of inducing the combination of nitrogen and hydrogen to an extent obtainable otherwise only by the action of a catalyst under a high pressure. The rate of flow of the nitrogen–hydrogen mixture through the capillary tube was measured by allowing the gas issuing from the reaction tube to pass through a small, specially constructed gas-washing bottle, in which the ammonia was absorbed by very dilute sulphuric acid, the number of bubbles which formed per minute being counted and the volume of a bubble being known. The estimation of ammonia in the resulting solution was carried out by means of Nessler's reagent.

It is difficult to estimate the temperature of the small high-tension arc formed, which, however, for the purpose of obtaining rough comparative figures for the various times of contact, has been assumed to be at approximately 3000°, but the effect of increasing temperature on the yield of ammonia formed is clearly seen. This rise in yield with increasing temperature at high temperatures (in contradistinction from the decrease obtained at moderate temperatures) agrees with the results already reported. When working with small spark-gaps, a considerable deposit of platinum, removed from the electrodes by volatilisation and other

means, was obtained on the sides of the capillary tube, and in some cases the tube became fractured by the intense local heat, although in general the tube itself remained moderately cool, and in any case showed no tendency to soften.

The above results having demonstrated the necessity for employing as small a spark-gap as possible, in order to obtain the maximum local heating effect and consequently the maximum yield of ammonia, the effect of varying the time of contact with a spark-gap of constant small length (0·5 mm. and 1·5 mm.) was investigated. With an exceedingly small arc of the nature described, sufficiently rapid cooling for the retention of the ammonia formed is readily obtained by the action of the tube itself, the difficulty being rather the uniform heating to arc temperature of the comparatively rapid current of gas.

Table III demonstrates this point, it being found that any increase in the time of contact of the gas with the small arc, within the limits studied, causes a corresponding rise in the ammonia-content of the issuing gas.

TABLE III.

	Spark-gap in mm.	Velocity of flow in c.c. per hour.	Estimated time of contact in seconds.	Percentage of ammonia by volume in issuing gases.
(*a*)	0·5	97·2	0·0006	0·7
	0·5	40·5	0·0015	1·1
	0·5	18·9	0·0032	1·4
	0·5	15·0	0·0041	1·5
(*b*)	1·5	670·0	0·00027	0·25
	1·5	130·0	0·0014	0·5
	1·5	64·8	0·0028	0·6
	1·5	34·8	0·0052	0·87

The above results appeared to offer considerable encouragement for the investigation of the formation of ammonia by rapidly cooled high-tension arcs of a larger size. The results of such work will be communicated in a later paper.

[*Received, March 21st*, 1918.]

XXXIII.—*Atomic and Molecular Numbers.*

By HERBERT STANLEY ALLEN.

ATOMIC NUMBERS.

ATOMIC weight and its determination have occupied a prominent position in the work of chemists since Dalton first put forward the Atomic Theory. Recent investigations in connexion with radio-

active elements and lead derived from radioactive substances have proved that the atomic weight has not the unique value hitherto attributed to it, and that a chemical element, such as lead, may be a mixture of "isotopes" occupying the same place in the periodic classification, but inseparable by chemical methods. Increasing importance is now being attached to the atomic number of an element, that is, the number which denotes the position of the element in Mendeléev's periodic table. As is well known, there are a few instances in which the place of the element is not in agreement with the atomic weight determinations; in such cases, the atomic number is given the value appropriate to the place in the table assigned by the chemical or physical properties. The values of the atomic numbers now accepted are given in table I, which follows the periodic classification of the elements commonly adopted. A better representation of the facts is obtained by employing a spiral in three dimensions. In this case, hydrogen may be placed at the pole of the spiral.

According to the electrical theory of matter, the atom consists of a central nucleus or core, carrying a resultant positive charge, surrounded by rings of negative electrons. It was first suggested by van den Broek that the number of the place in the periodic table was the same as the number of electrons in the atom or the number of unit charges carried by the nucleus. The same suggestion was made shortly afterwards by Soddy in connexion with the radioactive changes in the last thirteen places in the periodic table. The hypothesis is confirmed by the measurements of Barkla on the intensity of the X-radiation scattered from various substances. These indicate 7 electrons per atom of N, 8 for O, 6 for C, 16 for S, 1 for H. Rutherford's work on the scattering of α-particles by atoms of matter led him to the conclusion that the concentrated nuclear charge was approximately equal to half the atomic weight multiplied by the charge of an electron. The atomic numbers are, in fact, roughly equal to half the atomic weight.

It was, however, through the work of Moseley on the frequency of vibration of the X-rays, which are characteristic of the elements, that the importance of the atomic numbers was firmly established. The square root of the frequency of a line in the X-ray spectrum was found to be proportional to a number which increased by unity in passing from one element to the next in the periodic table. Thus every element from aluminium to gold may be characterised by an integer, N, which determines its X-ray spectrum. These atomic numbers were tabulated for the elements in question on the assumption that N for aluminium is 13. Between uranium and hydrogen, only five places remain vacant. For the rare earths,

PERIODIC SYSTEM OF THE ELEMENTS.

O	I	II	III	IV	V	VI	VII	VIII
	H 1							
He 2	Li 3	Gl 4	B 5	C 6	N 7	O 8	F 9	
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	
A* 18	K* 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26 Co* 27 Ni* 28
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	
Kr 36	Rb 37	Sr 38	Yt 39	Zr 40	Cb 41	Mo 42	—43	Ru 44 Rh 45 Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te* 52	I* 53	
Xe 54	Cs 55	Ba 56	The Rare Earths 57 —					
					Ta 73	W 74	— 75	Os 76 Ir 77 Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83			
Nt 86		Ra 88		Th 90		U 92		

* Elements not placed in the order of the atomic weights.

which have not been tabulated in table I, Moseley found the following values for N: La, 57; Ce, 58; Pr, 59; Nd, 60; Sa, 62; Eu, 63; Gd, 64; Ho, 66; Er, 68.

It may now be regarded as certain that most of the properties of the elements depend on the value of the atomic number rather than on that of the atomic weight. For example, the atomic frequency which determines the thermal behaviour of the element in the solid state has been shown by the author (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 100; *Phil. Mag.*, 1917, [vi], **34**, 478, 488) to bear a simple relation to the atomic number. Certain electronic frequencies are related to the atomic number in a similar way.

It will be noticed that Moseley's work does not give an unique determination of the value of N, since it is based on the assumption that N is 13 for aluminium. Rydberg has suggested that two unknown elements should be included in the periodic table between hydrogen and lithium, so that the atomic number of lithium would be 5 instead of 3. For all the elements later in the table, Rydberg's ordinals would be greater than Moseley's numbers by 2 units. Evidence in favour of Moseley's numbers is accumulating. Thus Barkla's results on the scattering of *X*-rays by air show that the number of electrons is as near to 7 for an atom of nitrogen as it is possible to estimate the pressure of the air under which the experiments were made. In the work of the present author on the relation between atomic frequency and atomic number, it was found that the atomic numbers of Moseley gave more satisfactory agreement than did the atomic ordinals of Rydberg. The same conclusion was arrived at by van den Broek (*Phil. Mag.*, 1914, [vi], **28**, 630).

The atomic numbers express in a compact form many facts that have been long familiar to students of chemistry. They afford a striking confirmation of the statement of Chancourtois, made in 1863: "The properties of the bodies (elements) are the properties of number." Newlands assigned to the elements numbers (from 1 to 56) to indicate the order in which the elements must be placed when arranged in the ascending order of their atomic weights. He put forward the "law of octaves," according to which the numbers for members of the same family will differ by 7, or some multiple of 7, provided that the elements are not consecutive. Newlands admitted that it might be necessary to alter the number (7) separating analogous elements to some higher figure should a large number of new elements be discovered (compare Garrett, "The Periodic Law," 1909, Ch. III.). An examination of the atomic numbers of table I shows that in many cases the difference between the numbers for members of the same family is either 8

or some multiple of 8. In other cases, however, the difference is found to be 18. Thus in the case of the inert gases of the zero group, the atomic numbers for He (2), Ne (10), A (18) show differences of 8, whilst A (18), Kr (36), and Xe (54) show differences of 18. The interval between Xe (54) and Nt (86) is $32 = 4 \times 8$. In the case of subsidiary families of the same group, a common difference of 10 is manifest, for example, K (19), Cu (29), or Rb (37), Ag (47). The reason for these variations from the more commonly observed difference of 8 is the presence of three elements (for example, Fe, Co, Ni) instead of a single element in Group VIII of the table. The two extra elements change the common difference from 8 to 10 or from 16 to 18. Thus the law of octaves must be replaced by a new rule, which may perhaps be termed the rule of eight—a rule, however, to which there are quite definite exceptions (1) in the consecutive elements of Group VIII, (2) in the elements displaced two units by Group VIII, (3) in the metals of the rare earths.

MOLECULAR NUMBERS.

The author has suggested the introduction of the term "molecular number" to signify the sum of the positive charges carried by the atomic nuclei contained in the molecule. Thus the molecular number bears the same relation to the atomic number as the molecular weight bears to the atomic weight. When a molecule contains *a* atoms of an element A, *b* atoms of B, and *c* atoms of C, its chemical formula may be written $A_aB_bC_c$, whilst its molecular number will be $N = aN_a + bN_b + cN_c$, where N_a, N_b, N_c are the atomic numbers of the component elements. For example, the molecular number of water (H_2O, hydrol) is 10, for the molecule contains two atoms of hydrogen (nuclear charge, 1) and one atom of oxygen (nuclear charge, 8). Thus the C.G.S. system of units is a decimal system in a deeper and more intimate sense than its originators supposed, for it is based on the assumption that the gram is the mass of 1 c.c. of water at the temperature at which its density is a maximum. This fact probably accounts for the remarkable numerical relations, involving powers of 10, which the author has shown to exist between certain fundamental physical constants (*Proc. Physical Soc. London*, 1915, **27**, 425).

The four compounds, CH_4, NH_3, H_2O, HF, formed by the combination of hydrogen with a "typical" element belonging to successive groups in the second series of the periodic table, all have the same molecular number, 10. The corresponding elements in the third series of the table form compounds with hydrogen of the

same type, SiH_4, PH_3, H_2S, HCl, all having the molecular number 18 (=10+8).

It may be remarked here that the molecular number is usually, but not invariably, an even number. This arises from the fact that when the valency is odd, the atomic number is usually odd also; but in the case of an element, such as copper, which may be either univalent or bivalent, or in the case of some of the metals of Group VIII the molecular number may be odd.

We have seen that the atomic numbers of analogous elements usually differ by 8 or a multiple of 8, or in some cases by a number that is 2 units greater than one of the foregoing. It is obvious that results of a similar character are to be expected in dealing with the molecular numbers of analogous compounds. The halogen compounds of the alkali metals may be considered by way of illustration. The results are collected in table II, the figures in italics being the differences between the molecular numbers in adjoining rows or columns.

TABLE II.

Element.	F 9 Fluoride.		Cl 17 Chloride.		Br 35 Bromide.		I 53 Iodide.
Li 3	12	*8*	20	*18*	38	*18*	56
	8		*8*		*8*		*8*
Na 11	20	*8*	28	*18*	46	*18*	64
	8		*8*		*8*		*8*
K 19	28	*8*	36	*18*	54	*18*	72
	18		*18*		*18*		*18*
Rb 37	46	*8*	54	*18*	72	*18*	90
	18		*18*		*18*		*18*
Cs 55	64	*8*	72	*18*	90	*18*	108

The molecular number of a cuprous haloid exceeds by 10 that of the corresponding potassium compound, and similarly the molecular number of a silver haloid exceeds by 10 that of the corresponding rubidium compound.

In the case of an element which has a valency greater than 1, the results may be more complicated, since one or more of the atomic numbers may require multiplication by a numerical factor depending on the number of atoms in the molecule. For compounds containing only elements from N=1 to N=25, however, comparatively simple results will be obtained, since the divergences due to the three elements in Group VIII do not then appear.

Instead of the law of octaves, we have what has been termed the rule of eight holding, with certain exceptions, in connexion with the molecular numbers of analogous compounds.

The value of N for a compound radicle can be calculated in the same way as for a complete molecule. Thus for the ammonium group (NH_4), the value of N, which may be called the group

number or the radicle number, is 11. It is noteworthy that this is the same as the atomic number of sodium, which can be replaced by the ammonium group in so many of its compounds. The principle here involved may be extended, and we may say that in a chemical compound one radicle may frequently be replaced by another having the same number, or a number differing from the first by 8 or a multiple of 8.

The hydrogen molecule, H—H ($N=2$), may be regarded as the typical simple molecule, from which a large number of chemical compounds may be derived by substituting for one or both of the hydrogen atoms another atom or radicle.

Thus water may be looked on as a typical compound in which one atom of hydrogen ($N=1$) is combined with the hydroxyl group, OH ($N=9$). The hydroxyl group may be replaced by CH_3, NH_2, F, for each of which $N=9$, giving rise to the compounds methane, ammonia, and hydrogen fluoride. Again, in each of these compounds the hydrogen atom may be replaced by one of the groups mentioned, giving rise to such compounds as C_2H_6, $CH_3\cdot OH$, N_2H_4, $NH_2\cdot OH$, H_2O_2, for which the molecular number is $9+9=18$.

Owing to the fact that the group number of $\cdot CH_2\cdot$ is 8, the rule of eight is prominent in the case of organic compounds. In open-chain compounds, the addition of each CH_2-group means an increase of 8 in the molecular number.

It is necessary to enter a caution as regards the interpretation of the results when dealing with a chemical group or radicle. The "group number" may be taken to represent the sum of the charges of the atomic nuclei of the group. It will only represent the number of negative electrons associated with the radicle as well when the radicle, considered as a whole, is not charged or electrically neutral. According to the views of Sir J. J. Thomson (*Phil. Mag.*, 1914, [vi], **27**, 768), the radicle may be charged either positively or negatively, and in such a case the number of negative electrons will differ from the radicle number here given.

The molecular numbers here discussed, and the relations between them, are not mere arithmetical curiosities. It is to be remembered that the molecular number is associated with a perfectly definite physical conception, namely, the number of unit charges found in the positive nuclei of the atoms in the molecule or the number of the complementary negative electrons. It is to be anticipated that the molecular numbers will play an important part in determining the physical or chemical characteristics of molecules or radicles. Some progress, in fact, has already been made in establishing such a connexion. It has been shown by Nernst and others that the thermal behaviour of a compound in

the solid state depends on a certain characteristic frequency or frequencies. The author has found (*Phil. Mag.*, 1918, [vi], **35**, 338) that simple relations exist between the products obtained by multiplying such a frequency and the molecular number of the compound. Thus there must be an intimate connexion between the specific heat and the molecular number. In the author's opinion, it is safe to predict that other physical properties of chemical compounds will be found to depend on the values of the molecular numbers.

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[*Received, January 18th*, 1918.]

XXXIV.—*Reactions between Solid Substances.*

By LESLIE HENRY PARKER.

IN a previous communication by the author (T., 1914, **105**, 1504), it has been shown that under certain conditions it is possible to bring about interaction between various pairs of solid substances by means of shearing stress, even at ordinary temperatures, or at least very greatly to increase the velocity of these reactions above that which normally pertains at these temperatures. The experiments described in that paper led the author to the conclusion that shearing stress, such as could be applied by hand between a pestle and mortar, is widely different in its effects from simple pressure, and that one of the main reasons why it is able to bring about reactions between apparently solid substances is that local or surface fusion of the reacting substances is occasioned.

This phenomenon seemed of sufficient interest to warrant further study, as it is a well-known fact that salts in the fused state are capable of reacting together.

In considering the conditions under which solid salt pairs are capable of reacting, it has to be remembered that most of the ordinary salts melt at a temperature that is high compared with that at which one commonly works with these substances; moreover, that a slight rise in temperature very often occasions a very rapid increase in the reaction velocity between two substances. From this it follows that the readiness with which two salts react in the fused state may be due to the influence of one or both of the following factors, namely, (1) the *high temperature* necessary

to bring one or both of the salts into a state of fusion, or (2) the existence of one or both of the salts in the *liquid state*, and the intimate contact occasioned thereby.

The object of the present investigation was to attempt to gain some idea of the relative importance of these two factors, because if high temperature is the main influence in causing two salts to react, some further agency must be looked for than mere fusion when reactions are brought about under shearing stress. If, on the other hand, the existence of the liquid state is the predominating influence, there appears to be no reason why salts should not react with appreciable velocity at ordinary temperatures should one or more of them be brought into a state of fusion, however transitory.

An investigation was therefore commenced on the velocity of reaction between various salt pairs at temperatures up to and through the melting point of the mixtures. The form of the curve obtained by plotting velocity of reaction against temperature should give information on the point desired.

Let us suppose that the temperature is the main influence in accelerating the velocity of reaction. The latter will go on increasing as the temperature rises until the melting point of the mixture is reached. At this point, however, there should be no marked increase in velocity, as we have assumed the existence of the liquid state to be of secondary importance. The curve should therefore exhibit no discontinuity at this temperature, but pass smoothly through the melting point.

On the other hand, let us suppose that the existence of the liquid state is of greater importance to the progress of the reaction. There may be, and probably will be, an increase of reaction velocity between the two mixed salts while still both in the solid state. When the point of fusion of the mixture is reached, however, there will be a sudden increase in the reaction velocity, and the curve will exhibit a sudden break at this temperature.

EXPERIMENTAL.

Sodium Carbonate and Barium Sulphate.

The interaction between these substances has already been investigated under shearing stress, as described in the previous paper (*loc. cit.*).

10·6 Grams of sodium carbonate, prepared from purified sodium hydrogen carbonate and dried by prolonged heating, were mixed with 23·34 grams (equivalent quantity) of barium sulphate, precipitated from purified barium chloride, and dried by heating in a current of dry air. The two salts were placed in a dry, air-tight

bottle, stirred with a glass rod, and shaken for fifteen minutes to mix them thoroughly. An arbitrary sample of this mixture was then taken for analysis.

A quantity equivalent to 1·06 grams of sodium carbonate (3·394 grams) was weighed out, treated with cold water, and lixiviated through a specially prepared Gooch crucible, the filtrate being treated with *N*- and *N*/10-hydrochloric acid, as previously described (*loc. cit.*). An amount of acid was neutralised corresponding with exactly 1·06 grams of sodium carbonate, showing that the original mixture was homogeneous and not affected by water. If sufficient care were taken to ensure that the salts were in a fine state of subdivision, and that they were stirred (not ground) and shaken together sufficiently, this method of sampling gave a similar result with many other experiments. No variation in the composition of the mixture in various parts was therefore to be feared, especially as only sufficient mixture was made up at any one time for nine experiments and one sample.

A nickel boat was then constructed to accommodate, when about half full, 3·394 grams of the mixture. This was heated to various temperatures for various lengths of time in an electric furnace, constructed by winding about 900 cm. of nichrome wire (4·1 ohms per metre) on 20 cm. of opaque silica tubing of 4·4 cm. internal bore. This was insulated with about six turns of asbestos paper and two turns of asbestos cloth. The ends were closed with asbestos card, and the whole was connected with a 110-volt lighting circuit, when suitable temperatures, as registered by a thermo-element, could be obtained and adjusted by variable resistances.

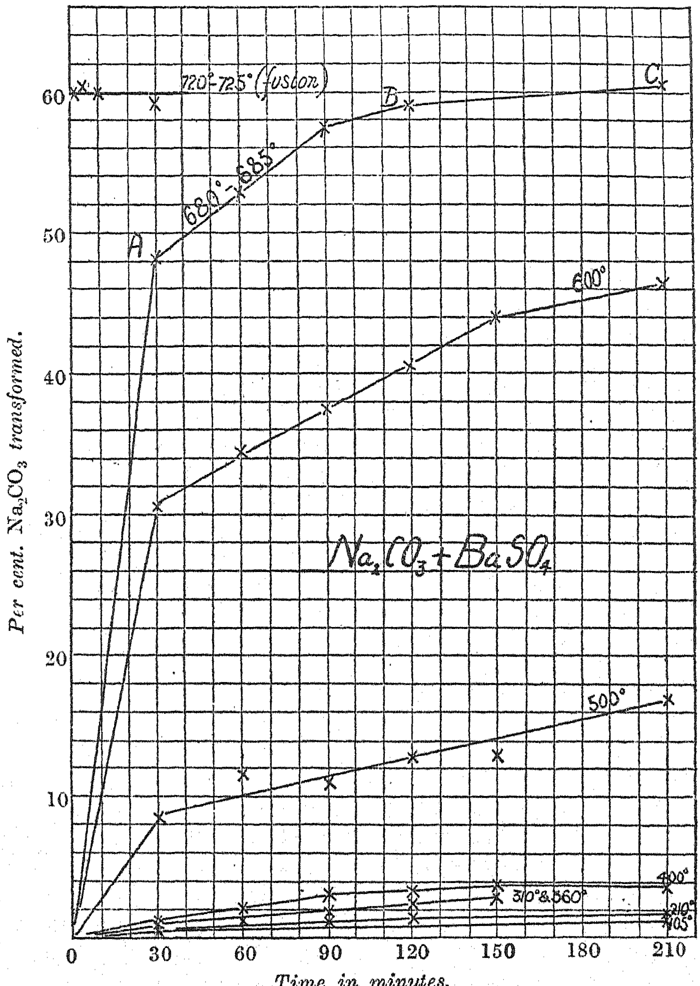
The procedure for each experiment was to heat the furnace to the required temperature, open one end, quickly insert the boat

TABLE I.

Time in minutes.	Sodium carbonate transformed. Per cent.							
	105°	210—215°	310°	360°	400°	500°	600°	680—685°
30	0·55	0·48	1·07	0·96	1·37	8·42	30·5	48·1
60	1·37	0·30	1·31	1·25	2·27	11·7	34·4	52·8
90	—	1·19	1·97	2·26	3·34	11·1	37·6	57·6
120	—	1·37	2·62	—	3·64	13·1	40·6	58·8
150	0·55	—	2·98	—	3·94	13·2	44·0	—
180	—	1·79	—	—	—	—	—	—
210	1·37	1·79	—	2·86	3·76	17·4	46·3	60·6
								700—720° (fusion).
2								60·0
5								60·6
10								60·0
30								59·2

containing the mixture, so adjusting its position in the middle of the furnace on some silica supports that it was clear of the walls of the furnace and almost touching the thermo-element, and close the furnace for the required time. At the expiration of a definite

FIG. 1.



period, the boat was withdrawn and the residual sodium carbonate was estimated. The results are shown in the table on p. 398.

These results are expressed graphically in Fig. 1.

It will be noticed that this mixture fuses at about 720° (as

registered by the thermo-element used), and in this state the velocity of reaction, so far as can be seen, is practically instantaneous, equilibrium being set up for the reaction

$$Na_2CO_3 + BaSO_4 \rightleftharpoons BaCO_3 + Na_2SO_4$$

when about 60 per cent. of the sodium carbonate is transformed.

It will also be remarked that up to 400°, the amount of sodium carbonate that has entered into reaction with the barium sulphate is insignificant, even after three and a-half hours. What little double decomposition has occurred has taken place fairly regularly, and it is fairly easy to compute the average reaction velocity for the temperatures up to 400°. The curves for 500°, 600°, and 685°, however, show some peculiarities. It will be noticed that during the first thirty minutes, in each case the reaction has started fairly rapidly, but after this time, has slowed down to a regular velocity, the points lying practically on a straight line.

This might be explained by the presence of a trace of moisture occluded in the particles of the salts, which is always very difficult to remove. At the high temperature of the experiments, this is rapidly expelled, but causes a certain amount of reaction between the salts on its own account. Once driven off, however, its influence is lost, and the straight part of the curve represents the true velocity of reaction between sodium carbonate and barium sulphate at any particular temperature.

It is possible that this moisture may have occasioned the small amount of change at the lower temperatures, and that had it been possible completely to dry the salts, the velocity of reaction up to 400° would have been negligible. In the curve for 685°, the portion between the points *A* and *B* has been taken as representing the reaction velocity, as the point *C* represents equilibrium, which was probably attained before the time represented in the figure (210 minutes). If we now plot reaction velocity against temperature, we obtain the curve shown in Fig. 2 (continuous line), which is remarkably regular up to the point for 720°, when, the velocity of the reaction at that point becoming instantaneous, a sudden break in the continuity of the curve occurs.

If the equilibrium of this system is considered, it will be seen that in the solid state there are present four solid phases, which can be defined by three components. This gives one degree of freedom for the system, and the equilibrium is therefore determined by the temperature; it is therefore probable that there is a definite equilibrium mixture for each temperature, and that the lower curves in Fig. 1 would not all of necessity approach the equilibrium attained on fusion, namely, the transformation of 60 per cent. of the sodium carbonate.

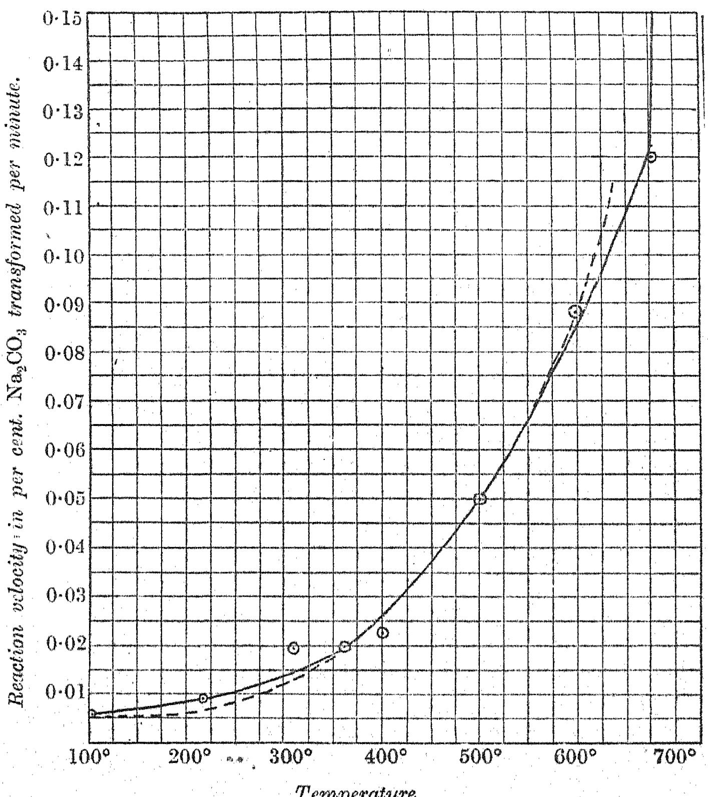
It was also endeavoured to reconcile the velocity–temperature curve in Fig. 2 with the formula put forward by Arrhenius and van't Hoff, namely,

$$\frac{d \log k}{dT} = \frac{A}{T^2} + \frac{B}{T} + C.$$

The dotted curve in Fig. 2 is that given by the formula

$$\log k = \frac{1988}{T} + 11{\cdot}24 \log T - 36{\cdot}332.$$

FIG. 2.



which follows the experimental curve very closely except at the higher temperatures as the point of fusion is approached.

The next two cases were chosen to be of such a nature that no limiting equilibrium could be obtained, it being possible for the reaction to proceed to completion in one sense.

Silver Nitrate and Sodium Carbonate.

The products of this interaction are silver carbonate and sodium nitrate, and as the former is unstable, decomposing with rapid evolution of carbon dioxide at 100°, the rate of evolution of this gas from a mixture of silver nitrate and sodium carbonate could be used as a measure of the velocity of reaction between these two salts. The reaction may be regarded as capable of proceeding to completion in the sense

$$Na_2CO_3 + 2AgNO_3 = 2NaNO_3 + Ag_2CO_3,$$

as the only equilibrium which can be established is that between silver oxide and carbon dioxide, which may be neglected.

Silver nitrate crystals were purified by recrystallisation from dilute nitric acid solution and dried by heating just above the fusion point for two hours. The sodium carbonate was prepared and purified as before. The apparatus employed in these experiments consisted of a thick Jena-glass test-tube, somewhat longer than the electric furnace used to heat it, with a tube of soft glass ground into its open end. This tube was sealed to the gauge column of a Sprengel exhaust pump. The mixture of silver nitrate and sodium carbonate (always 1·699 grams of the former and 0·53 gram of the latter) was placed in a porcelain boat, which was then introduced into the Jena-glass tube. This was then connected to the pump, the apparatus exhausted, and the Jena-glass tube and contents were heated by the electric furnace. The rate of fall of the manometer on the pump was noted, giving a measure of the velocity of reaction proceeding between the mixed salts. The salts were tested for occluded gases by being heated separately in a vacuum. No appreciable fall in the mercury was to be noted. In any series of readings taken at any particular temperature, after the last reading the tube and contents were allowed to cool to the ordinary temperature, when the manometer was again read, and all previous readings for that experiment were corrected accordingly, thus eliminating the effect of the various temperatures on the partial pressure of the carbon dioxide. The results are shown in the table on p. 403.

These results are expressed graphically in Fig. 3.

The characteristics previously noted are again in evidence. After a short period of induction over the first five minutes, due no doubt to the gradual heating up of the mixture, the curves for the temperatures between 110° and 170° show an increasing rapidity for the reaction at the start, over a period of about a

TABLE II.

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.					
	90°	110°	130°	155—160°	165°	170°
10	—	—	0·5	1·8	2·7	15·3
15	—	—	—	—	12·6	30·6
20	—	—	4·5	12·9	22·4	42·3
25	—	—	—	—	28·6	50·4
30	1·0	5·5	9·5	20·2	34·0	53·7
60	1·8	12·7	17·2	32·2	43·8	63·0
90	3·7	15·8	20·0	37·7	48·3	69·3
120	—	17·0	—	41·4	52·8	—
150	5·5	18·0	29·0	45·0	57·4	77·4
180	—	19·0	29·0	46·0	60·0	81·0
210	8·2	—	—	—	—	—
270	9·6	—	—	—	—	—
300	10·5	—	—	—	—	—

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury.	
	180° (fusion).	240—250° (fusion).
5	3·2	1·8
6	7·2	3·7
7	13·6	6·4
8	25·4	10·1
9	59·7	14·7
10	97·0	26·6
10½	112·0	43·1
11	125·0	62·4
11½	135·0	89·0
12	146·0	114·0
12½	157·0	134·0
13	168·0	153·0
13½	180·0	170·0
14	191·0	186·0
14½	202·0	205·0
15	211·0	221·0
15½	219·0	237·0
16	225·0	
16½	230·0	
17	235·0	
17½	239·0	
18	243·0	
19	247·0	

further fifty minutes. After that time, the rate of reaction in each case becomes practically uniform.

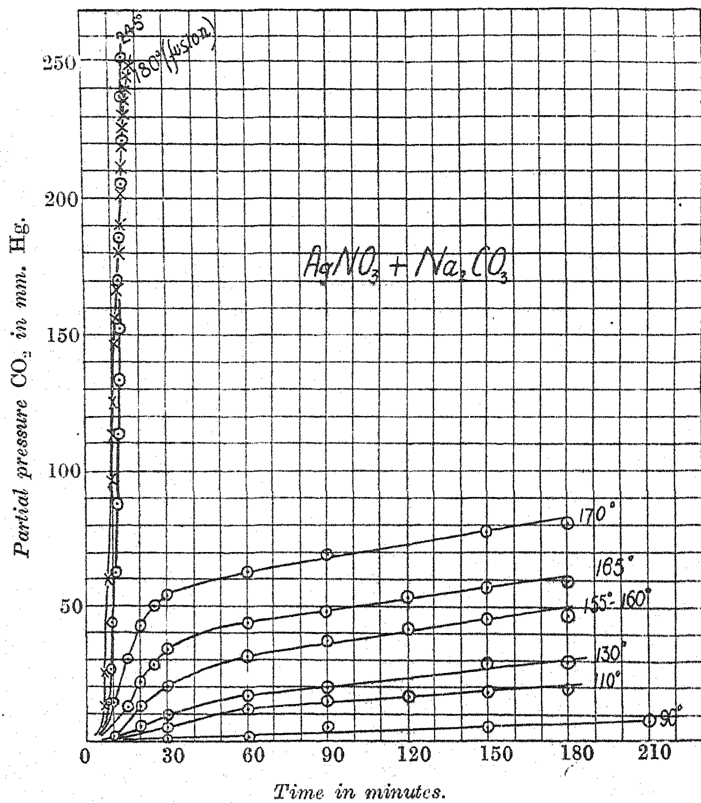
The curves for 180°, where fusion took place, and for 245°, although apparently almost coincident on the diagram at the scale given, are by no means so in reality. Calculated from the figures in table II, the curve for 245° represents almost twice the reaction velocity as does the curve for 180°.

The graphical representation of reaction velocity against tempera-

ture is shown in Fig. 4, and again a sudden increase is to be noted at the temperature of fusion.

In the solid state, there are here present five phases, comprised of four solid phases ($AgNO_3$, Ag_2O, $NaNO_3$, Na_2CO_3) and one gaseous phase (CO_2); all these are defined by the four components Ag_2O, Na_2O, N_2O_5, and CO_2. The pressure of the system is there-

FIG. 3.



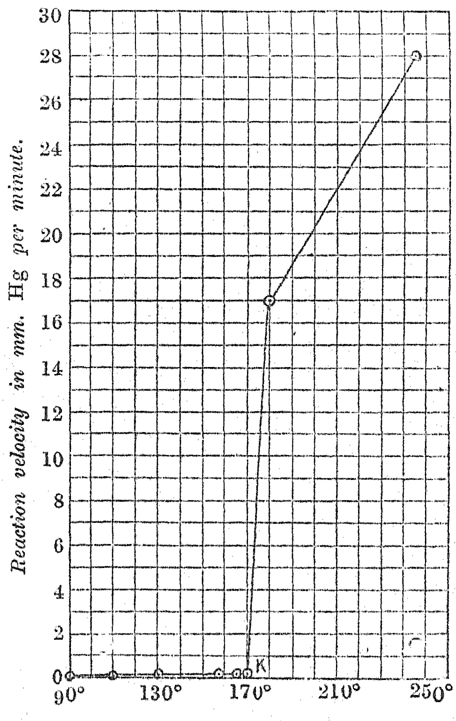
fore a function of the temperature, an example of the active masses of the reacting substances remaining constant in the solid state.

In the partly fused state there exist four solid phases, one liquid phase, and one gaseous phase, with the same number of components as before. There are, therefore, no degrees of freedom, and the point K is analogous to the triple point in the system ice-water-water vapour.

Cuprous Chloride and Sodium Carbonate.

This mixture was chosen more from the point of view of discovering what happened after fusion than actually at the fusion point. The cuprous chloride was prepared from the commercial substance by dissolving it in concentrated hydrochloric acid and pouring the solution into water. The precipitated salt was quickly

FIG. 4.



collected, washed with alcohol and ether, and dried for many hours at 100°.

It remained quite white, apparently indefinitely, in a dry, airtight bottle. For each determination, a mixture of 0·991 gram of this salt with 0·53 gram of sodium carbonate was taken (equivalent quantities), and the experiments were conducted with the same apparatus as in the last reaction. The results are shown in the following table.

TABLE III.

Time in minutes.	Corrected partial pressure of carbon dioxide in mm. of mercury. 100°	150°	200°	260°
5		3·3	1·8	3·6
10		7·5	8·2	48·0
11		—	—	83·0
12		—	—	116·0
13		—	—	147·0
14		—	—	174·0
15		10·0	20·0	199·0
16		—	—	217·0
17		—	—	234·0
18		—	—	249·0
19		—	—	259·0
20		13·3	38·0	268·0
25		—	59·0	310·0
30		15·8	77·0	336·0
40		17·5	97·5	376·0
50		20·0	113·0	—
60		20·8	127·0	419·0
90		25·0	164·0	—
120		—	195·0	—
150		—	208·0	—
180	nil	—	230·0	—

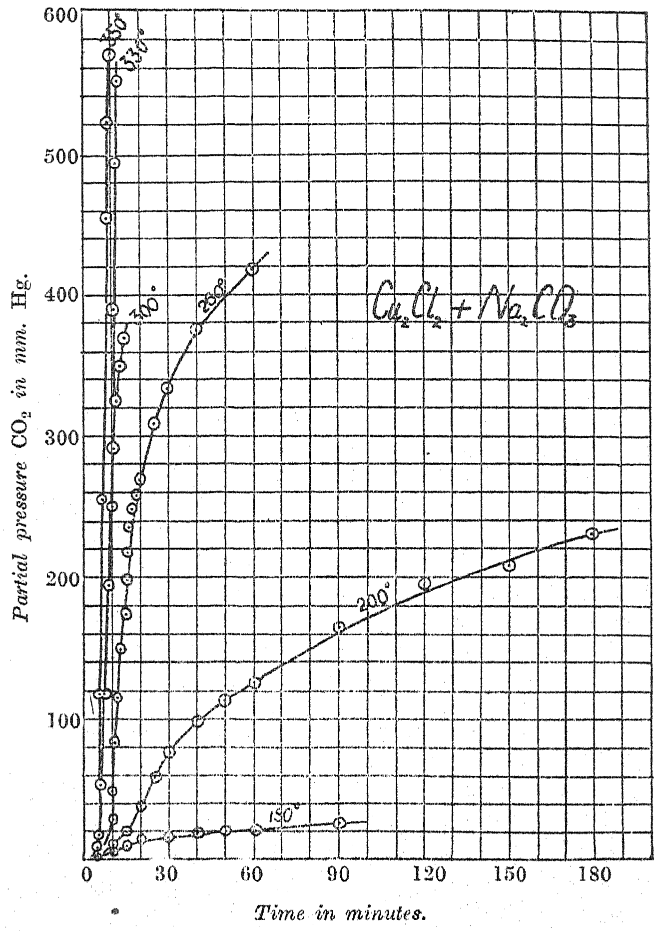
	300°	330°	350°
5	7·3	17·5	9·2
6	18·4	24·0	35·0
6½	—	35·0	68·0
7	53·0	53·0	119·0
7½	83·5	84·0	178·0
8	119·0	123·0	256·0
8¼	138·0	141·0	307·0
8½	155·0	163·0	353·0
8¾	172·0	181·0	404·0
9	192·0	200·0	454·0
9¼	207·0	217·0	—
9½	223·0	238·0	521·0
9¾	237·0	258·0	—
10	250·0	281·0	569·0
10¼	262·0	306·0	—
10½	274·0	334·0	—
10¾	283·0	361·0	—
11	291·0	389·0	—
11¼	—	420·0	—
11½	309·0	446·0	—
11¾	—	471·0	—
12	324·0	497·0	—
12¼	—	515·0	—
12½	338·0	531·0	—
12¾	—	548·0	—
13	350·0	—	—
13½	362·0	—	—
14	370·0	—	—

These results are expressed graphically in Figs. 5 and 6.

Fusion took place at about 260°, causing a large increase in the reaction velocity.

It seems fairly well established, therefore, that the process of fusion of itself causes a marked increase in the reaction velocity of the mixtures, the ratio of velocity in the liquid state to that at the highest temperature in the solid state varying from infinity

FIG. 5.

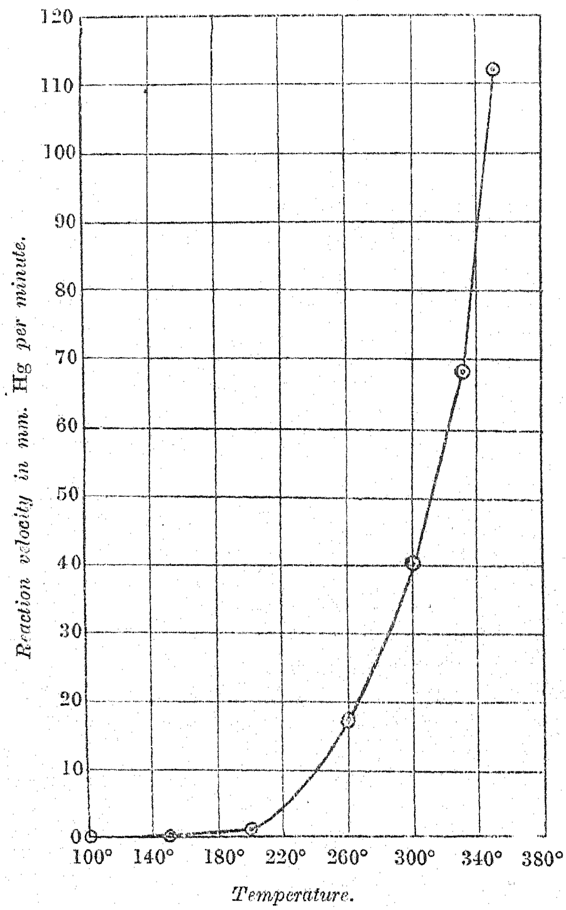


in Case 1, through about 150 in Case 2, to about 20 times in Case 3.

It may be taken, therefore, that the liquid state *per se* has a direct bearing on the interaction of salt pairs. It should be noted, however, that after fusion the velocity of reaction is not quite so

independent of the temperature as in the solid state. The velocity becoming practically infinite on fusion in Case 1, this could be investigated no further, but in Cases 2 and 3 it is seen that further rise in temperature causes a further great increase in reaction velocity, although not nearly so great as the increase pro-

FIG. 6.



duced by fusion over the velocity in the solid state. In Case 2, a rise of 65° nearly doubles the reaction velocity, and in Case 3, a rise of 90° multiplies the rate about six times. The reacting molecules now being in intimate contact, the temperature begins to exert a well-defined influence.

There seems therefore to be no inherent objection to the explanation, put forward in the previous communication, of the reactions brought about by shearing stress between apparently solid substances, namely, that the stress causes local or surface fusion of the salts; it has been shown that the liquid state, quite apart from temperature effects, has an important bearing on the capacity for interaction.

It is known that the size of particle may have a slight influence on the melting point of a substance, as in the case of salol investigated by Pavlov (*J. Russ. Phys. Chem. Soc.*, 1910, **40**, 1022), who showed that the temperature of fusion was, however, only lowered 2·8° for one hundred times the increase of surface (ten times decrease of radius). This therefore is probably a factor of no great magnitude.

Tammann (*Ann. Phys. Chem.*, 1899, [ii], **68**, 553, 629) showed that simple pressure was capable of influencing the melting and transition points of a large number of substances. He also showed (*Zeitsch. physikal. Chem.*, 1903, **46**, 818) that the fusion curve for sodium sulphate rose to a maximum at a pressure of 750 kilos. per sq. cm., and then fell considerably.

Most inorganic salts, however, have their fusion points raised by increase of pressure, and even in cases of the reverse, such as that of silver bromide, it is necessary to apply pressures of the order of 10^5 atmospheres to cause fusion at ordinary temperatures. Although the experimental facts do not yet seem to offer a complete explanation of the action of shearing stress as applied to solid substances, it thus appears probable that such stress has a peculiar action of its own towards the production on the surface of such materials of a state analogous to, if not identical with, fusion.

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
ROYAL COLLEGE OF SCIENCE. [*Received, March 11th*, 1918.]

XXXV.—*The Association of Organic Compounds in Benzene and Alcohol Solution as Determined by the Vapour Pressure Method.*

By WILLIAM ROSS INNES.

IN a previous paper (T., 1902, **81**, 682), the author has described the results obtained in an investigation on the influence of temperature on association in benzene solution by Raoült's ebullioscopic method.

The investigation was undertaken chiefly with the view of discovering the cause of the very different behaviour of the acids and oximes on the one hand, and the anilides, alcohols, and phenols on the other, in hydrocarbon and other solvents, generally spoken of as associating solvents.

It seemed probable that if the different behaviour of these two classes of compound could be explained, some light would be thrown on the nature of association.

As is well known, the acids and oximes give data in dilute solution which indicate that the molecular weight is normal at extreme dilution; with increasing concentration, the value for the molecular weight rises, at first rapidly, then more slowly, until it reaches double the normal value; further increase of concentration affects the value but little in most cases.

Anilides, alcohols, and phenols behave quite differently, the molecular weight increasing, generally, almost linearly, and there is no indication of the molecular weight reaching a limit, even at the highest concentrations at which it is usual to carry out determinations by the cryoscopic and ebullioscopic methods.

The investigation failed in its main objective, and it was evident that more concentrated solutions would have to be examined in order to arrive at the desired result.

The reverse problem, namely, the behaviour of substances belonging to "the associating group of solvents" in alcohol, also seemed worthy of investigation.

It was decided to use the vapour-pressure method in this investigation. If the experimental results obtained by Raoult in ethereal solution by the vapour-pressure method are plotted to show molecular weight against concentration, the regularity of the curves, apart from the determinations in dilute solution, suggests that the statical method used is much more accurate than references to it in literature would lead one to suppose, and that little is needed to make it a satisfactory one.

It was originally intended to use the statical method. With Ramsay and Young's apparatus (*Phil. Trans.*, 1887, **178**, 57), the temperature could be varied over a wide range, and it was hoped, by boiling out the tube and stirring the solution, so as to prevent varying concentration at the free surface by evaporation or condensation of the solvent, that accurate results would be obtained. While the pressure apparatus was being made, the experiments described in the following pages were commenced, and the method gave such satisfactory results that it was continued until other work prevented the completion of the investigation.

The apparatus employed was essentially the same as that used in the ebullioscopic method (T., 1902, **81**, 685), except that the jacket of the boiling tube was not connected to the constant pressure apparatus, but to a separate reservoir with manometer and pump, so that the temperature of the jacket could be kept approximately at the temperature employed. A temperature about 3° higher than that of the boiling tube was aimed at. For the experiments at 75°, alcohol boiling under atmospheric pressure was used. The tube *L* of the regulator was graduated, so that the apparatus could be set to give the pressure required, and was fitted with a micrometer screw allowing of ready adjustment to 0·1 mm. or less. A barometer, trapped to prevent entrance of air to the upper part, stood in the same trough as the manometer *H*, and the difference in height was read on a millimetre mirror scale. This difference is, of course, the pressure in the apparatus, and is independent of the atmospheric pressure. A set of thermometers reading to 0·1° with open scale, made by Hicks, was used. They were not calibrated, as they were employed merely as zero instruments. That they were accurate and that the zero altered very little is shown by the vapour pressures obtained for benzene and alcohol at different temperatures. The exact temperatures are, of course, given by the vapour pressure of the solvent. In order to prevent changes of pressure affecting the volume of the thermometer bulb, the thermometer was placed in a tube fitting it closely and containing enough mercury to cover the bulb.

The boiling tube was of such size that from about 15 to 50 grams of solution could be used. It was of lead glass, and no platinum was fused through the bottom. It was packed with beads and platinum clippings, as already described (T., 1901, **79**, 262). The end of the condenser of the boiling tube was connected to a tube dipping into a fractionating flask to act as a trap in case of sudden frothing, and the side-tube of the fractionating flask passed into a drying tube which joined on to the constant-pressure apparatus. In order to obtain satisfactory results, it was found necessary to

take every possible precaution to exclude traces of moisture from the apparatus and chemicals.

The benzene used contained a trace of thiophen, it was of perfectly constant boiling point, and was dried over phosphoric oxide. The alcohol was finally dried with phosphoric oxide and distilled. It was of constant boiling point. The benzene and alcohol were kept in bottles, through the corks of which pipettes passed, the upper end of the pipette passing into a drying tube. The solvent was measured out in all cases.

Most of the substances were bought in a sufficient state of purity for use; a few were further purified. The dimethyl tartrate and β-benzilmonoxime were prepared. The substances were in most cases melted and cast in a glass tube. When solid, the tube was heated and the rod of substance pressed out. β-Benzilmonoxime could not be satisfactorily treated in this way and did not form pastilles readily; it was partly melted, allowed to cool, and broken into pieces of suitable size. The substances were prepared for use a day in advance and kept in a vacuum over sulphuric acid until required.

Method.

The boiling tube containing the solvent is connected to the constant-pressure apparatus, the regulator set to give approximately the pressure required, and the apparatus exhausted. When the pressure has fallen and the regulator begins to act, the gas is lit and adjusted to such a height that the benzene boils briskly. It is essential that boiling should be fairly rapid, otherwise in concentrated solutions layers of different concentration form and cause very large errors. After the solvent has been boiling for a few minutes, the regulator is altered until the temperature is that required (t°), and the apparatus left for an hour; if necessary, a further adjustment is then made, the barometer and manometer are read, and boiling is continued for a further ten minutes. If temperature and pressure are both constant, the first addition of solute is introduced in the manner already described (*loc. cit.*), the regulator being altered so as to lower the pressure by the amount which it is expected the vapour pressure will be lowered. When solution is complete, the pressure is altered until the temperature (t°) is again obtained, and the solution allowed to boil for ten minutes; a further adjustment is made if necessary, and the solution allowed to boil for a further ten minutes until constancy is obtained; the pressure is then read. Additions are then made under similar conditions until the concentration is about 50 per cent.

Beyond 50 per cent., very large additions have to be made to increase the concentration in the steps required. A fresh series was then started with 10 c.c. of solvent. The pressure of the solvent was determined as before, sufficient solute added to give a concentration of 50—60 per cent., and the additions continued as before up to 80 per cent.

In some cases, where only one series was carried out at a given temperature, 15 c.c. of benzene were used, and, after determining the vapour pressure, sufficient solute was added to cover completely the thermometer bulb. A range of concentration from about 15 to 70—80 per cent. was thus attained in one series. Beyond 80 per cent., determinations were made by weighing into the boiling tube a suitable amount of solute, a small amount of benzene was added, and the vapour pressure determined after the temperature had become constant; further additions of benzene were then made. In order to do this, the clip *p* was closed, the flame under the boiling tube removed, and the addition of benzene made with a long pipette. Before reopening the clip *p*, the pressure in the apparatus is increased considerably by opening the cock *e*, otherwise frothing would occur, and the clip is opened gradually to avoid loss of benzene vapour as much as possible. The regulator is moved to give a higher pressure, and the flame put back. At 75°, the pressure was allowed to become equal to the atmospheric. In this way, it was possible to work from a concentration of 95 per cent. downwards. At the highest concentration, a constant temperature was not attained. With azobenzene there was a very slow variation of a few tenths of a degree about a mean position. The determination took a very long time, owing to the extreme slowness of the temperature change. The method is not a practical one at a concentration of 95 per cent.; at 90 per cent., however, the difficulty almost entirely disappears with azobenzene as solute. Only two substances were examined at these concentrations, namely, the "normal" azobenzene and the very abnormal dimethyl tartrate. The determinations with dimethyl tartrate at these great concentrations were much more difficult than with azobenzene, especially in the determinations above 60 per cent. molecular concentration at 75°. The only method by which determinations could be made was to follow the change of temperature with corresponding change of pressure until the temperature remained constant for a time. In this way, a higher and lower limit of the vapour pressure was obtained. Owing to the slowness with which the temperature altered and the variation in the limit, it was not practicable to take a mean. The largest pressure, that is, the pressure corresponding with the highest molecular weight, was

taken in each case. Although the possible error in these determinations is large and not much value can be attached to the individual values, it seems fair to assume that the real molecular weights are not greater than those calculated.

At 53°, the temperature variation was much less than at 75°, and single determinations were carried out instead of series, so that the variations could be observed over sufficient time to take a mean. Even under these conditions, the experimental error appears to be large, the two determinations at nearly the same concentration showing a large difference in molecular weight.

In the determination at 63°, the temperature remained almost constant throughout the time ordinarily devoted to a series.

There seems little doubt that the variation of temperature in these experiments is due to the difficulty with which the benzene, returned from the condenser, mixed with the highly viscous solution, whilst the greater constancy at the lower temperatures may be due partly to the more efficient stirring of the larger bubbles of vapour formed at the lower pressure and partly to the smaller amount of benzene vapour condensed for similar rates of boiling.

Results.

The results obtained are given in tabular form on p. 430 *et seq*.

Col. I. gives the temperature at which the series was carried out, as indicated by the thermometer $= t$.

II., the observed pressure of the solvent, no corrections being made $= p$.

III. $p - p'$, also without any correction.

IV., weight of solvent actually taken $= G$.

V., weight of solute $= g$.

VI., grams of substance per 100 grams of solution

VII., the percentage molecular concentration, $100n/n + N$.

VIII., the molecular weight found $= m'$.

IX., the association factor m'/m.

In calculating VI., VII., VIII., 0·4 gram is subtracted from the weight of the solvent in the experiments at the higher pressures and 0·3 gram in those at the lower pressures, to allow for the amount of solvent in the state of vapour and that wetting the walls of the tube above the solution.

The vapour-pressure method offers the advantage that a series of determinations at different concentrations can be carried out isothermally, whilst the great simplicity of the vapour pressure law for concentrated solutions of "normal" substances suggests that it will be easier to interpret the experimental results obtained

with more complex systems, where present-day theory offers little guide, than would be the case by the cryoscopic, ebullioscopic, or osmotic methods.

The vapour pressure law was first established experimentally by Raoult for non-volatile solutes in a volatile solvent, and was shown by him to apply satisfactorily for a number of solutes in ethereal solution even up to 80—90 per cent. concentration. It is, however, from the study of mixtures in which both constituents are volatile that the accuracy of the law has been experimentally established. It has been shown that for mixtures of non-associated, closely related liquids, the so-called ideal solutions, the law holds with great accuracy and within the limit of experimental error throughout the whole range of concentration from 0—100 per cent.

Raoult's law $\frac{p-p'}{p} = \frac{n}{N+n}$ is readily transformed algebraically into (2) $\frac{p-p'}{p'} = \frac{n}{n}$ and (3) $p' = p\frac{N}{N+n}$, on the assumption that n has the same value in both numerator and denominator, the last form being that most convenient for considering solutions in which both constituents are volatile, whilst (2) is a convenient form for calculating the results obtained with non-volatile solutes.

Where both constituents are volatile, it is evident that the distinction between solute and solvent entirely disappears, since for each constituent its partial pressure is proportional to the product of its pressure in the pure state and its molar fraction in the solution. The same must be true where the vapour pressure of one of the constituents of the solution is negligibly small, since this is merely a limiting case of the more general relation. It is therefore purely arbitrary which constituent we call solvent and which solute. In this communication, that constituent which separates in the pure state—as vapour in the vapour-pressure and ebullioscopic methods, as ice in the cryoscopic method—is referred to as the solvent, whatever its concentration in the solution.

The vapour pressure law has been deduced thermodynamically by several methods for two classes of solutions, namely, ideal solutions of any concentration and infinitely dilute solutions.

In deducing the law for ideal solutions, one of the simplifying assumptions that has to be made is that the constituents of the solution are not associated as pure liquids, and that no association takes place on mixing them. It is evident that the law thus derived becomes purely empirical when applied to associated solutions. That such an assumption has to be made does not show that the vapour pressure law is not applicable where association is

present; the assumption is merely a mathematical convenience. It seems reasonable to assume, for purposes of investigation and in absence of any evidence to the contrary, that if all the more chemical factors, association, ionisation, and solvation, are allowed for, the law will hold for any solution, and that the physical quantities which enter into the thermodynamic equation will be allowed for automatically, since these quantities are undoubtedly functions of the more chemical factors.

Although it is not at present possible to deduce the general laws for lowering of vapour pressure and freezing point, raising of boiling point, etc., we know that these laws are interconnected by a series of rigid thermodynamic differential equations which are independent of concentration, ionisation, association, and solvation, and can therefore be certain that general qualitative conclusions drawn from results obtained by one of these methods can be applied in discussing the results of any of the other methods, whether association, solvation, etc., occur or not.

The vapour pressure law can be deduced for dilute solutions without making any assumption as to the molecular aggregation of either solute or solvent, or as to whether solvation occurs. The only assumption necessary for thermodynamic treatment in this case is that the solution is infinitely dilute.

This method of derivation gives no information as to whether the law applies where association of the solute occurs, since we know as the result of a very large number of experimental determinations that zero association is always indicated at infinite dilution.

As regards solvation, it follows that where this occurs, the solvated complex behaves as a single molecule at infinite dilution, and it is reasonable to assume that in more concentrated solution the law is observed if the quantity of solvent solvated at a given concentration is subtracted from the total solvent.

It also follows from the method of deriving the law for dilute solutions, that in the vapour pressure relation $\frac{p-p'}{p}=\frac{n}{N+n}$. N, the number of molecules of the solvent, is that corresponding with the normal molecular weight, whatever degree of association the solvent may have in the liquid state.

The evidence that the solution laws hold when association takes place is at present purely experimental, and rests on the formation of definite complexes by organic acids and oximes in a number of solvents. In the present communication, it is shown that formanilide and acetanilide also form definite complexes.

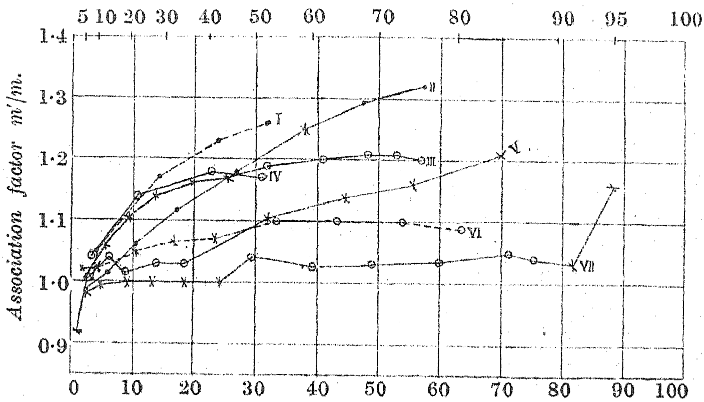
Benzene as Solvent.

The results obtained with a number of substances which did not show a great departure from Raoult's law are shown graphically in Fig. 1. Determinations belonging to different series on a curve are distinguished by circles, crosses, or dots.

It will be seen that there is a break in several of the curves where the series at lowest concentrations (5—50 per cent.) meets the next series (60—80 per cent.), and is naturally most marked where the curve is approximately straight. The break is obviously due to some form of experimental error in the second series,

FIG. 1.

Percentage concentration for azobenzene.



Percentage molecular concentration 100 $n/N+n$.

I. Formyldiphenylamine.
II. Phenanthrene.
III. Benzil.
IV. Hexadecyl alcohol.
V. Methyl salicylate.
VI. Benzophenone.
VII. Azobenzene.

amounting sometimes to from 3 to 4 per cent., and apparently constant throughout the series. The cause of this error is not at all obvious.

One of the substances, azobenzene, obeys Raoult's law absolutely within the limit of experimental error.

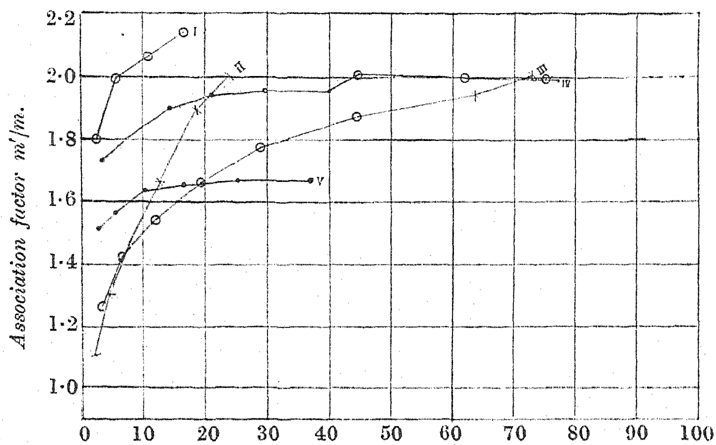
All the other substances show more or less association in concentrated solution. From the degree of their abnormality, the general conclusion may be drawn that those groups which cause slight but distinct association in dilute solution of the compounds of lowest molecular weight containing them, also cause a slight association in concentrated solution with compounds of such high

molecular weight that they do not show appreciable association in dilute solution, and, further, that the laws which connect the constitution of the solute with degree of association for the larger abnormalities in dilute solution also apply to the smaller abnormalities in concentrated solution.

Phenanthrene shows slight abnormality by both the cryoscopic and ebullioscopic methods; it is not therefore surprising that it shows distinct association in concentrated solution. The abnormality is, however, of interest, as on general grounds

FIG. 2.

Acids and oximes in benzene at 75°.



I. Cinnamic acid.
II. β-Benzilmonoxime.
III. Acetophenoneoxime.
IV. Phenylacetic acid.
V. *d*-Camphoroxime.

phenanthrene might be expected to form an ideal solution with benzene.

Acids and Oximes.

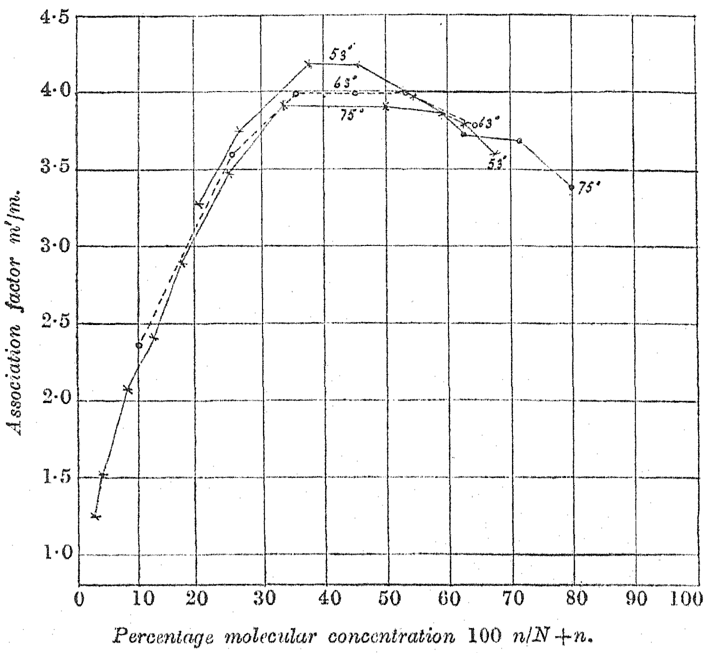
β-Benzilmonoxime, acetophenoneoxime, and phenylacetic acid all show a maximum association factor of 2. β-Benzilmonoxime was not sufficiently soluble to carry the series further (Fig. 2).

Cinnamic acid shows a decided tendency to give a higher molecular weight than that corresponding with the double formula; it seems probable that this is due to the presence of a double bond in the molecule. The solubility was not sufficient to carry the series further. *d*-Camphoroxime shows a rapid increase in associa-

tion up to 10 per cent., but only reaches a maximum of 1·66, and has almost this value over a range of 27 per cent. By the cryoscopic method in benzene, association factors approaching 2 are obtained even in 5 per cent. solution. In naphthalene (m. p. 80°), on the other hand, its behaviour is very similar to that in benzene at 75°, and it gave an association factor of 1·6 at a concentration of 10·50 grams per 100 grams of solvent (Innes, *Diss.*, Heidelberg, 1896, p. 42), the highest concentration at which it was examined.

FIG. 3.

Formanilide in benzene.



The low maximum would therefore seem to be connected with the temperature at which the determinations were carried out.

Anilides.

The results obtained with formanilide are shown graphically in Fig. 3.

Series of determinations were made at 75°, 63°, and 53°.

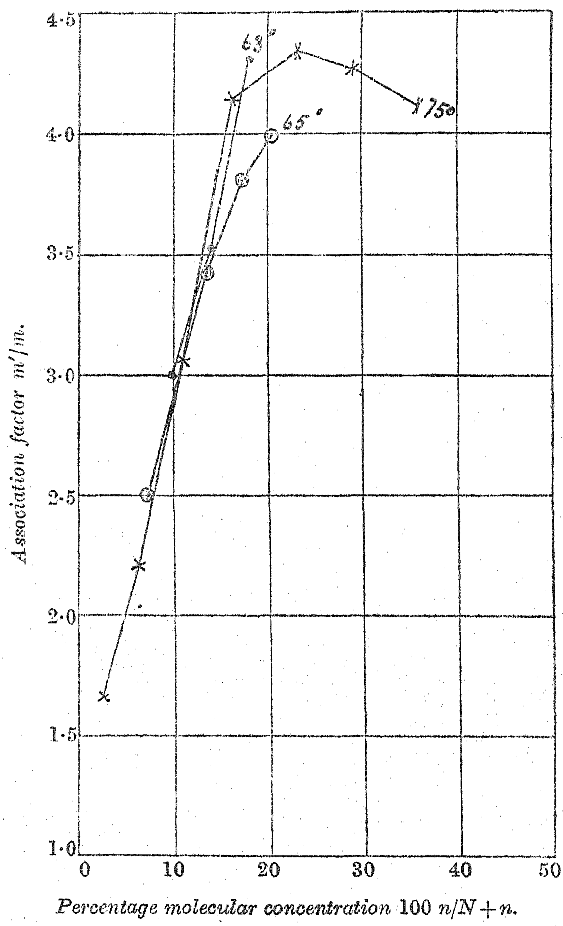
The constancy of the association factor over a considerable range of concentration at 75° and 63°, as well as the small temperature

effect on the maximum, points to the formation of a definite molecular complex containing four simple molecules.

Acetanilide gives a curve at 75° similar to that of formanilide, but the rate of association is still more rapid (Fig. 4).

FIG. 4.

Acetanilide in benzene.



At 63° the solubility is considerably less than at 75°; at both temperatures, the solution of highest concentration is nearly saturated. The series at 63° was repeated at 65°, as a doubt was felt as to whether the whole of the solute was in solution in the last determination at 63°. With the exception of this determina-

tion, the curves at 63° and 65° are either practically identical with that at 75° or below it, indicating an increase of association with increase of temperature.

Since increase of association with increase of temperature is improbable, and the values at 63° and 65° fall well on the same curve, it seems possible that the series at 75° is affected by experimental error.

Taken by themselves, the values obtained with acetanilide do not point to the formation of a definite molecular complex, but the fact that there is not more difference in the maximum values of acetanilide and formanilide, although the concentrations at which they reach this maximum are so different, does indicate that such a complex is formed. There seems to be a slight tendency to further association, as with formanilide at 53°.

Dimethyl Tartrate.

This substance, containing two hydroxyl groups, is extremely abnormal. Its behaviour in dilute solution at different temperatures has already been investigated (Innes, *loc. cit.*). In concentrated solutions, it shows the characteristic alcohol type of curve up to concentrations approaching 50 per cent. molecular, and the influence of temperature both on the rate of increase of association and on the maximum association is most striking. There is no evidence of the formation of a definite molecular complex (Fig. 5).

The values obtained beyond equimolecular concentration at 63° and 53° suggest that the molecular weight would be normal at 100 per cent., and that the shapes of the upward and downward curves on each side of equimolecular concentration are either identical (apart from experimental error) or very similar. Lines of equal slope are shown dotted in the figure. The values obtained at 75° are not consistent with this being the case, but, as has already been pointed out, the probable error in these series, at high concentrations, is much greater than at the lower temperatures.

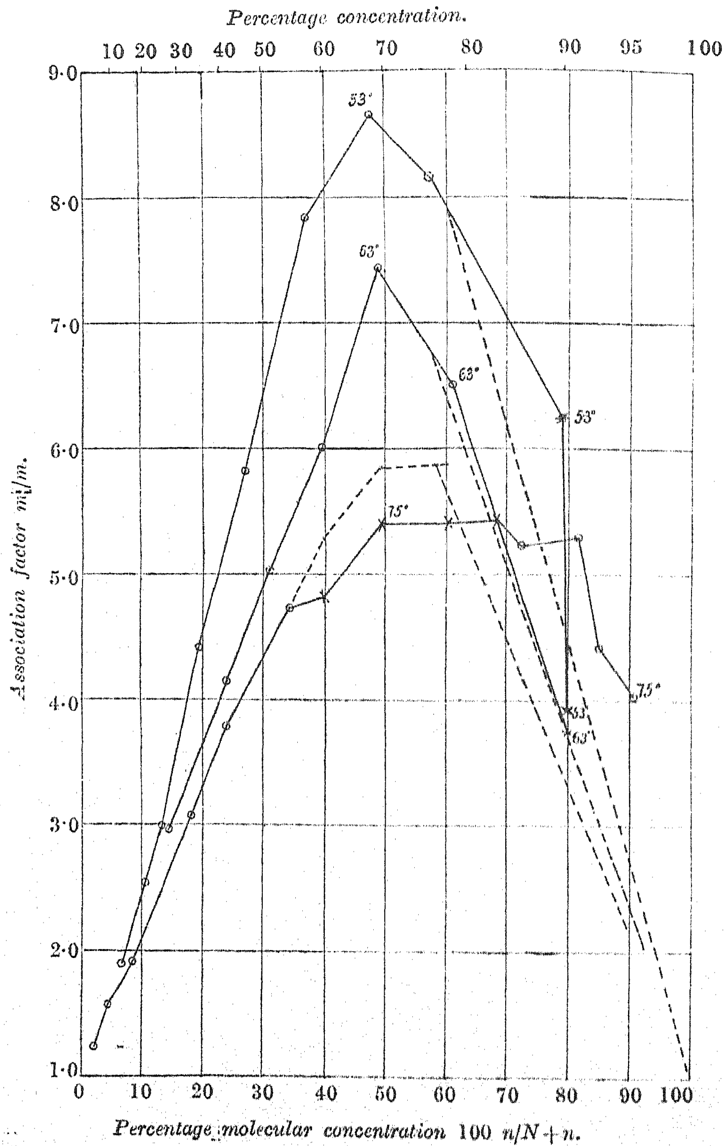
Ethyl p-*Hydroxybenzoate.*

This substance, the only abnormal phenol examined, was unfortunately of limited solubility. The first two determinations show a very rapid increase of association, and the line joining them is almost linear with the intersection of the co-ordinates. With increase of concentration, the rate of increase of association diminishes rapidly, the shape of the curve indicating that a maxi-

mum would be reached with an association factor between 2·8 and 3. As the solubility would be less at lower temperatures, it seemed useless further to examine this substance.

FIG. 5.

Dimethyl tartrate in benzene.



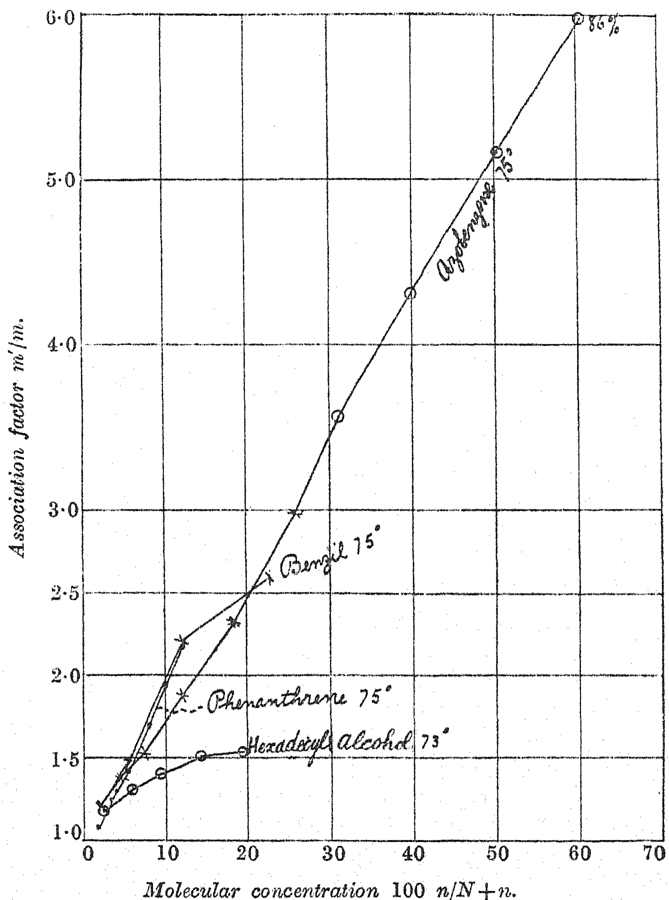
Alcohol as Solvent.

Four substances were examined in alcohol, and all were found to give abnormal molecular weights (Fig. 6).

Phenanthrene and benzil give practically identical molecular

FIG. 6.

Alcohol as solvent.



weights at equal molecular concentrations up to the limit of solubility of phenanthrene, and the rate of increase is nearly linear and very rapid. The last determination with benzil shows a decreasing rate of association.

Azobenzene is also extremely abnormal; it gives values for the molecular weight somewhat smaller than those with benzil and phenanthrene at the same molecular concentration, and the rate of increase is at first slightly less, then slightly greater, than linear. The last four determinations (63·2 to 85·9 per cent.) are exactly linear, and when produced to zero concentration, give the normal molecular weight with considerable accuracy.

Hexadecyl alcohol is about twice as abnormal as in benzene.

The view is very generally held that organic solutes should show less tendency to association in alcohol than in benzene, since the conductivity of electrolytes in benzene is extremely small, whilst in alcohol their conductivity is considerable, and it has been assumed that a substance with dissociating power for electrolytes would not favour the formation of complex molecules. If we admit this view, it might be argued that the abnormalities in alcoholic solution are not due to association. The fact that three substances of such different constitution as azobenzene, phenanthrene, and benzil should all be highly abnormal and to almost the same extent over a considerable range of concentration, whilst in benzene, in concentrated solution, they behave so differently, also suggests that the abnormality is not due to the solute, *per se*, but to some specific action of the solvent. It therefore seems advisable to consider the possible ways in which the solvent could exert an influence on the apparent molecular weight.

That associated liquids, such as alcohol, have an abnormally low vapour pressure has been well established (Vernon, *Chem. News*, 1891, **64**, 54; Young, *Phil. Mag.*, 1892, [v], **34**, 507; T., 1893, **63**, 1251; van't Hoff, "Lectures," Part 3, 50). It is also known that, in solution, alcohol is non-associated at sufficient dilution, whether in an inert or in an associating solvent.

If, therefore, we add to alcohol a miscible, inert, non-volatile liquid, the vapour pressure of the alcohol will not be that corresponding with its molar fraction, but will be larger by an amount which is a function of the dissociation of the complex molecules of the alcohol. An abnormally small lowering of the vapour pressure will therefore be obtained. The effect of the smaller lowering of the vapour pressure will be to increase p' and decrease $p-p'$ in $m=\frac{gMp'}{G(p-p')}$, and both these influences will increase the apparent molecular weight. With such an inert solute, in a solvent the liquid molecules of which are associated, but not the vapour molecules, we should expect to get values for the molecular weight of the solute, which point to the normal molecular weight at extreme dilution, and increase with concentration at a rate which is a

function of the dissociation of the complex molecules of the solvent. Hexadecyl alcohol might be expected to be such an inert solute with respect to alcohol, since it appears to be a general rule that substances of constitution similar to that of the solvent give normal molecular weights in that solvent. The departure of hexadecyl alcohol from Raoult's law may therefore be attributed to the progressive dissociation of the alcohol as it is diluted with the hexadecyl alcohol, and the much greater abnormality of the other substances must be sought in some other influence.

When there is combination between the solute and solvent, it is evident that part of the solvent is removed from the solution and no longer functions as solvent. G is therefore decreased, and at the same time p' will be decreased owing to the increased concentration of the solute complex, and $p-p'$ increased. The decrease of G and p' and the increase of $p-p'$ would all act in the direction of decreasing the molecular weight. It is further evident that the influence of such combination will become very great as the concentration approaches $n=N$, provided the compound or complex formed does not exert a decided vapour pressure.

After the experiments described in this paper had been carried out, the apparatus was used by Mr. B. C. Burt, who determined the vapour pressure of concentrated sulphuric acid solutions (T., 1904, **85**, 1345). His results, when suitably plotted (Fig. 7), show in a most striking manner the influence of combination between solute and solvent in molecular weight determinations in concentrated solutions.

Burt determined the vapour pressure of solutions ranging from 25 to 95 per cent., and calculated the molecular weights by Raoult's formula, using Regnault's values for the vapour pressure of water. The experimental figures at 100° were used when available; at the higher concentrations, it was necessary to take results at higher temperatures. As the influence of temperature at these high concentrations is very small, the form of the curve cannot be seriously affected. The curve of molecular weight against percentage concentration shows the influence of $n=N$ most clearly. There is first a rapid, then a slower fall until $n=N$ is reached, after which the molecular weight is practically constant and almost zero.

Since, in a solution in which the solute is practically non-volatile and the solvent readily volatile, any chemical compound formed must have a much smaller vapour pressure than that of the solvent, it is evident that, in such solution, combination between solvent and solute cannot occur if the normal or a high molecular weight is indicated at or near equimolecular concentration.

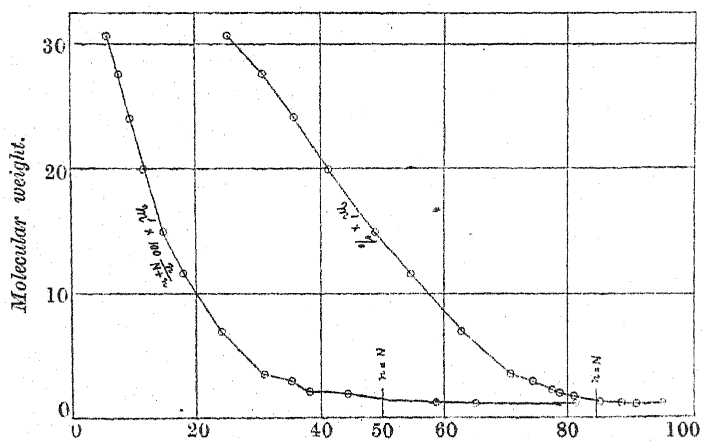
Since neither the dissociation of the solvent nor combination

between solute and solvent will explain the great abnormality of phenanthrene, benzophenone, and azobenzene in alcohol, it can only be supposed that the abnormality is due to association, and it follows *that alcohols and the "associating solvents" exert an associating influence on each other.*

Alcohol was first used as an ebullioscopic solvent by Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 454), and from his results in this and other solvents, he drew the conclusion that solvents like the alcohols, organic acids, and phenols, containing hydroxyl groups, are "dissociating solvents of the water type," and consequently complex molecules are not formed in them. Nernst lent support to Beckmann's hypothesis, by the theory that the higher

FIG. 7.

Apparent molecular weight of sulphuric acid (1) *against molecular concentration,* (2) *against percentage concentration.*



the dielectric constant of a solvent, the greater will be its power to split up double molecules.

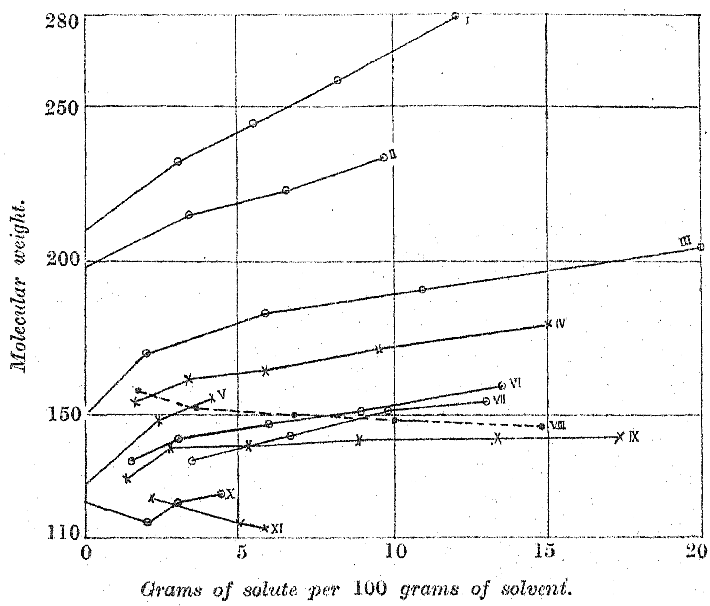
It is of interest to examine the experimental results on which Beckmann founded his theory. These are shown graphically in Fig. 8 for alcoholic solutions, molecular weights being plotted against concentration. Carbamide and racemic acid have not been included, the former because it was only examined in dilute solution, the latter because the values are irregular.

A glance at the curves will show that, with the exception of the acids, all the substances show a much more rapid increase of molecular weight than is shown by "normal" substances in benzene or naphthalene. Benzil, phenyl benzoate, ethyl benzoate,

and naphthalene, substances belonging to the "associating type" of solvent, are very abnormal; borneol, acetophenoneoxime, and acetanilide, belonging to the "water type," are less abnormal, and the curves of the last three substances are approximately parallel. If the view already brought forward, that the abnormality of hydroxy-compounds in alcohol is due to the dissociation of the

FIG. 8.

Beckmann's results in alcohol by the ebullioscopic method.



I. Benzil, 210.
II. Phenyl benzoate, 198.
III. Ethyl benzoate, 150.
IV. Borneol, 154.
V. Naphthalene, 128.
VI. Acetanilide, 135.
VII. Acetophenoneoxime, 135.
VIII. Tartaric acid, 150.
IX. Salicylic acid, 138.
X. Benzoic acid, 122.
XI. Succinic acid, 118.

alcohol complex, is correct, these curves should be parallel for equal molecular concentrations.

Succinic and tartaric acids show a decreasing molecular weight with concentration; evidently this is due to ester formation and combination of the water formed with the solvent. The normal molecular weights with salicylic acid must be attributed to a balance between the abnormality due to the dissociation of the solvent and that due to ester formation.

Beckmann's results therefore lend strong support to the deduction that there is mutual association between alcohols and substances of the hydrocarbon type.

Beckmann's classification into two types is still useful, however, and it is proposed to call the "associating solvent" type of substance *Carbotype*, and the "water type" of substance *Oxytype*, without, however, assuming any sharp line of demarcation between the two classes.

Numerous instances have been published of the comparatively normal behaviour of hydroxylated compounds and anilides in ethyl and methyl alcohols, but very few instances of association in alcohol, apart from those in Beckmann's paper, appear to have been observed. The following have been found (Peddle and Turner, T., 1911, **109**, 696):

m-Dinitrobenzene, 2·6—5·5, 1/100 gram-mols, per 100 c.c., $m' = 181—211$, $m = 168$.

Diphenylamine, 3·79—5·99, 1/100 gram-mols. per 100 c.c., $m' = 190—206$, $m = 169$.

Phenanthrene, 1·94—11·99 grams per 100 grams of solvent, $m' = 183—226$ (Behrend, *Zeitsch. physikal. Chem.*, 1892, **10**, 279).

Numerous salts, inorganic and organic, have been examined ebullioscopically in alcohol, and many of these show association as well as the influence of combination with the solvent (Turner and Pollard, T., 1914, **105**, 1751).

The close similarity in behaviour between the alcohols and phenols in solvents of the hydrocarbon type suggests that phenols and carbotype substances should also show mutual association. Robertson (T., 1906, **89**, 567) has shown that the hydrocarbons are highly associated in phenol solution, also that carbon tetrachloride is as abnormal as the hydrocarbons. Ethylene dibromide and bromoform are also abnormal, but to a less extent. The mutual association of the abnormal phenols and substances of the carbotype group must therefore be considered to be a general phenomenon.

The degree of abnormality of the substituted phenols follows definite laws as regards the nature and position of the substituting group, and the anilides follow similar laws. There seems little doubt, therefore, that a carbotype solute will give abnormal molecular weights in an anilide, and that mutual association takes place in this case also. Anilides do not seem to have been used as cryoscopic solvents, although formanilide (m. p. 46°) would be a convenient substance to use.

If mutual association takes place with acids and oximes in a carbotype solvent, it is obvious that no direct evidence of this

being the case can be obtained from the behaviour of a carbotype solute in an acid or oxime if the acid or oxime is associated to a double molecule in the liquid state.

There is, however, evidence that during the association of an acid or oxime in a carbotype solvent, the solvent exerts a specific influence on the association of a nature which has not been explained. If the solvent merely acted as a diluent, the mass law should apply to the dissociation of the double molecules, as in gaseous dissociation. Auwers (*Zeitsch. physikal. Chem.*, 1907, **60**, 385) has shown that with acids and oximes this is by no means the case, C_1^2/C decreasing very rapidly with concentration.

The data obtained in the present investigation are more suitable for such calculations than those used by Auwers, since the determinations were made isothermally; the results of calculation are, however, similar. The anilides also show large variations in the value of C_1^4/C.

Since there is direct and fairly conclusive evidence of mutual association between alcohols and phenols and a carbotype, it is reasonable to ascribe the influence of the carbotype solvent on the association of the acids, oximes, and anilides to the same cause.

The position of the maximum association of dimethyl tartrate in benzene at or near equimolecular concentration evidently indicates that in this instance association of solute and solvent takes place at the same rate. Although there is no evidence as to the rate of association of the solvent in other instances, it is not unreasonable to assume, for purposes of further investigation, that in a solvent which is non-associated in the liquid state, association of solvent and solute is in general equal.

The cause of mutual association of solute and solvent obviously cannot be chemical, as anything in the nature of combination between the two constituents, in concentrated solution, is impossible (p. 425). The only adequate explanation which has occurred to the author is that it is electrical in character.* It seems reasonable to suppose that the association begins in the oxytype substance, whether this is functioning as solvent or solute. If we imagine that for each molecule entering into an aggregate a definite quantity of electricity passes to the carbotype substance, causing in it an association equal to that in the oxytype, and that this goes on until an equilibrium is attained, depending on the temperature, concentration, pressure, and nature of the solvent and solute, this would account for the fact that dimethyl tartrate and benzene appear to associate at the same rate.

* That association may be due to electrical, not chemical, forces has already been suggested by Turner and English (T., 1914, **105**, 1793).

If we assume that the charge that passes when a substance associates is one electron per molecule, the charge per aggregate must be considerable when the association reaches 6—10, as with dimethyl tartrate. It might therefore be supposed that the molecules would arrange themselves in a definite geometric arrangement depending on their mutual attractions and repulsions, and that they would resist any influence which tended to alter this arrangement. The high viscosity of associated solutions would thus be explained.

Benzene as Solvent.

Azobenzene, $C_{12}H_{10}N_2 = 182$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'	m'/m.
75°	64·98	1·69	17·8	1·059	5·72	2·54	178	0·978
		3·34		2·193	11·2	5·12	181	0·995
		6·05		4·185	19·3	9·28	182·5	1·002
		8·72		6·30	26·6	13·3	182·5	1·002
		11·98		9·19	34·55	18·5	182	1·000
		15·78		13·02	42·9	24·2	182	1·000
75	65·09	18·89	8·9	8·54	49·7	29·8	189	1·042
		25·12		12·98	60·1	39·3	187	1·026
		31·30		19·18	69·0	49·0	188	1·030
		38·19		29·52	77·4	59·6	188	1·035
		45·69		49·56	85·2	71·3	191	1·050
		48·49		60·78	87·6	75·2	189	1·039
75	65·10	56·94	2·66	44·72	95·0	88·2	212	1·16
		53·3	4·435		91·8	82·1	187	1·03
		48·15	7·10		88·6	73·5	181	0·995

Benzophenone, $C_{13}H_{10}O = 182$.

72°	58·84	1·27	22·19	1·144	4·98	2·20	185·5	1·02
		3·62		3·422	13·56	4·54	186	1·02
		6·23		6·321	22·4	11·03	191	1·05
		9·49		10·42	32·3	17·0	194	1·065
		12·95		15·52	41·7	23·4	195	1·07
75	65·18	20·27	8·90	9·98	53·6	33·3	200	1·10
		26·55		15·17	63·7	43·1	200	1·10
		33·36		23·25	73·0	53·9	201	1·10
		40·07		34·95	80·4	63·5	198	1·09

Benzil, $C_{14}H_{10}O_2 = 210$.

75	65·02	0·59	22·19	0·567	2·53	0·955	202	0·92
		1·72		1·622	6·94	2·68	213	1·013
		3·46		3·517	13·9	5·65	224	1·067
		5·68		6·18	22·0	9·52	232	1·105
		8·04		9·38	30·0	13·7	239	1·140
		11·35		14·43	40·9	20·1	244	1·16
		14·80		20·27	48·2	25·6	246	1·17
75	65·17	18·53	8·90	10·94	56·1	32·0	250	1·19
		23·85		16·06	65·2	41·0	252	1·20
		28·22		21·42	69·2	48·1	254	1·21
		31·57		26·32	75·2	53·1	254	1·21
		34·27		30·88	78·3	57·1	522	1·20

Benzene as Solvent—(*continued*).

Formyldiphenylamine, $C_{13}H_{11}ON=197$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m
75	65·21	1·46	17·8	1·015	5·51	2·26	198	1·005
		2·72		2·017	10·40	4·39	208	1·05
		5·21		4·229	19·6	8·81	218	1·105
		8·35		7·562	30·2	14·73	230·5	1·17
		12·41		12·69	42·1	24·25	242	1·23
		17·76		20·79	54·5	32·2	249	1·26

Methyl Salicylate, $C_8H_8O_3=152$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m
75	64·90	1·71	22·19	1·176	5·10	2·69	153	1·005
		4·05		2·944	11·92	6·49	158	1·04
		5·65		4·171	16·06	8·94	155	1·015
		8·81		6·871	23·9	13·9	156·5	1·03
		11·70		9·822	31·05	18·7	160	1·05
75	65·18	42·85	4·45	18·83	82·1	70·0	185	1·21
		33·81	8·01		71·1	55·6	177	1·16
		26·89	12·46		60·9	44·4	174	1·14
		21·8	17·8		52·0	32·4	168	1·105

Phenanthrene, $C_{14}H_{10}=178$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m
75	65·13	1·74	22·19	1·340	5·80	2·62	175	0·984
		3·94		3·242	12·95	6·11	180·5	1·101
		6·62		6·002	21·6	10·8	189	1·060
		10·39		10·57	32·6	17·5	199	1·118
		15·61		18·63	46·2	27·2	211	1·18
75	65·14	21·18	8·90	11·82	58·0	37·8	223	1·25
		26·62		17·56	67·3	47·3	230	1·29
		32·98		26·59	73·5	57·6	235	1·32

Hexadecyl Alcohol, $C_{16}H_{34}O=242$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m
75	65·24	1·09	22·2	1·029	4·50	1·49	217	0·90
		2·04		2·261	9·40	3·24	251	1·04
		4·19		5·008	18·7	6·87	260	1·07
		6·34		8·30	27·6	10·92	276	1·14
		9·58		13·38	38·0	16·5	278	1·15
		13·24		20·245	47·1	23·0	285	1·18
		18·06		30·23	58·2	30·9	284	1·17

Cinnamic Acid, $C_9H_8O_2=148$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m
75	64·94	1·07	17·8	0·999	5·73	2·94	263	1·78
		1·96		2·024	10·43	5·77	291	1·965
		3·66		4·074	18·95	11·0	306	2·06
		5·92		7·10	28·95	16·5	316	2·14

Benzene as Solvent—(continued).

Phenylacetic Acid, $C_8H_8O_2=136$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m',	m'/m.
75	65·26	1·29	17·8	1·059	5·73	3·36	236	1·73
		2·62		2·274	11·54	6·95	244	1·79
		5·23		5·032	22·4	14·2	258	1·90
		7·94		8·13	31·8	21·1	263	1·935
		11·79		13·07	42·8	30·0	265	1·95
		16·57		20·08	53·6	39·8	265	1·95
75	65·51	18·56	8·9	12·06	58·5	44·8	280	2·06
		29·74		24·53	74·2	62·0	270	1·99
		40·23		44·86	84·0	75·2	259	1·90

Acetophenoneoxime, $C_8H_9ON=135$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m',	m'/m.
75	65·12	1·70	17·8	1·013	5·50	3·26	169·6	1·26
		3·09		2·127	10·91	6·60	192	1·42
		5·33		4·132	19·2	12·04	208	1·54
		8·19		7·174	29·2	19·25	224	1·66
		12·15		12·21	41·2	28·9	239	1·77
		19·43		23·92	57·9	44·4	252	1·87
75	65·20	37·5	4·43	19·31	82·4	72·9	269	1·99
		31·15	6·65		75·4	63·8	261	1·94

γ-Benzilmonoxime, $C_{14}H_{11}O_2N=225$; m. p. 113—114°.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m',	m'/m.
75	65·30	1·16	17·8	1·046	5·69	2·03	259	1·15
		2·09		2·167	11·11	4·15	295	1·31
		3·62		4·36	20·0	8·00	333	1·475
		5·20		7·34	29·7	12·71	397	1·68
		7·13		11·63	40·1	18·72	425	1·89
		8·87		15·81	47·6	23·98	450	2·00

l-d-*Camphoroxime*, $C_{10}H_{17}ON=167$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m',	m'/m.
75	65·16	1·22	17·8	1·072	5·80	2·80	252	1·51
		2·29		2·125	10·90	5·40	261	1·56
		4·33		4·316	19·9	10·4	272	1·63
		6·96		7·375	29·7	16·5	276	1·65
		10·99		12·54	41·9	25·2	278	1·66
		17·33		21·96	55·6	37·2	272	1·625

Formanilide, $C_7H_7ON=121$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m',	m'/m.
75	65·20	1·21	22·19	0·795	3·51	2·28	150·5	1·245
		1·78		1·482	6·36	4·19	189	1·562
		2·73		3·014	12·12	8·19	247	2·04
		3·63		4·812	18·1	12·45	293	2·42
		4·28		6·897	24·0	16·93	353	2·91
		5·60		10·99	33·5	24·43	422	3·48
		7·41		17·03	43·9	33·4	475	3·93
		10·39		25·02	54·6	50·3	473	3·91
		14·10		35·99	62·3	58·9	466	3·86

Benzene as Solvent—(*continued*).

Formanilide, $C_7H_7ON=121$—(continued).

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	65·14	11·71	8·90	10·98	56·1	45·1	454	3·74
		15·64		15·82	64·8	54·1	454	3·74
		19·88		21·92	71·8	62·3	250	3·72
		26·85		33·05	79·5	71·4	428	3·53
		35·23		53·23	86·3	80·0	410	3·38
63	43·53	1·87	13·3	2·137	14·1	9·58	288	2·36
		3·74		6·817	34·4	25·25	436	3·60
		5·33		11·14	46·3	35·5	479	3·96
		7·41		16·65	56·2	45·2	486	4·02
		9·70		22·75	63·7	52·9	476	3·94
		14·19		36·87	73·7	64·6	458	3·78
53	30·28	2·10	13·3	4·924	27·4	19·6	396	3·27
		2·62		7·130	35·4	26·1	451	3·74
		3·78		12·07	48·0	37·4	508	4·19
		5·07		16·92	56·6	45·6	505	4·18
		6·99		23·97	64·9	54·4	480	3·96
		9·27		33·65	72·2	62·7	458	3·79
		11·05		41·64	76·4	67·4	435	3·60

Acetanilide, $C_8H_9ON=135$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	64·96	1·36	17·8	1·070	5·76	2·43	224	1·66
		1·83		1·931	10·0	6·03	299	2·21
		2·45		3·628	17·2	10·8	414	3·06
		2·86		5·79	24·9	16·1	563	4·17
		4·20		9·05	34·2	23·1	586	4·34
		5·73		12·45	41·7	29·2	576	4·26
		7·87		17·18	49·7	36·2	557	4·12
63	43·60	1·55	22·2	4·18	16·0	9·93	404	2·99
		1·94		6·23	22·2	14·1	480	3·55
		2·16		8·43	27·8	18·2	580	4·30
65	46·58	1·39	22·2	3·041	12·2	7·41	354	2·62
		2·04		5·895	21·2	13·40	461	3·42
		2·48		7·96	26·6	17·45	507	3·76
		2·92		9·95	31·2	20·6	532	3·95

Dimethyl Tartrate, $C_6H_{10}O_6=178$.

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	64·97	1·08	17·8	0·853	4·66	2·1	226	1·22
		1·97		1·829	9·54	4·62	262	1·47
		2·97		3·524	14·7	8·15	342	1·92
		3·69		5·94	25·4	13·03	441	2·48
		4·33		8·78	33·5	18·1	550	3·08
		4·99		12·59	41·9	24·0	677	3·80
		6·57		20·78	54·5	34·3	826	4·64
75	65·20	6·59	8·90	8·50	49·7	30·4	687	3·86
		7·82		12·92	60·0	39·8	860	4·82
		10·00		19·27	69·1	49·6	966	5·43
		14·3		29·89	77·6	60·5	966	5·42
		18·41		42·32	83·2	68·5	976	5·49

Benzene as Solvent—(continued).

Dimethyl Tartrate, $C_6H_{10}O_6=178$—(continued).

t	p	$p-p'$	G	g	Per cent.	$100\,n/N+n$.	m'.	m'/m.
75	65·18	46·25	2·76	55·71	95·8	90·9	725	4·07
		36·67	4·54		92·9	85·2	796	4·47
		30·06	5·85		91·2	81·8	930	5·22
		20·83	9·70		85·8	72·4	995	5·60
63	43·63	2·56	13·3	5·443	29·5	15·5	524	2·94
		3·09		9·37	41·8	23·9	739	4·15
		3·56		13·22	50·5	30·8	895	5·02
		4·16		19·27	59·6	39·4	1099	6·17
		4·92		28·08	68·4	48·6	1324	7·44
		8·47		46·42	78·3	61·0	1155	6·50
63	43·53	24·53	4·43	45·35	91·5	80·3	664	3·72
53	30·23	1·04	13·3	2·053	13·4	6·47	338	1·89
		1·31		3·416	20·8	10·3	452	2·54
		1·53		4·69	26·4	13·6	528	2·97
		1·56		7·14	35·4	19·3	788	4·42
		1·81		11·00	45·8	26·9	1038	5·83
		2·07		17·09	56·7	36·5	1395	7·84
		2·88		26·07	66·8	46·9	1540	8·66
		4·23		39·4	75·2	57·1	1453	8·16
53	30·2	11·4	6·65	54·46	89·6	79·1	1113	6·25
53	30·2	15·4	6·21	54·68	90·3	80·2	694	3·9

Ethyl p-*Hydroxybenzoate*, $C_9H_{10}O_3=166$.

75	65·16	1·18	17·8	0·900	4·91	2·38	219	1·32
		1·97		2·017	10·4	5·17	290	1·75
		3·21		4·299	19·8	10·4	372	2·24
		4·70		7·48	30·0	16·8	430	2·59
		7·10		12·47	41·7	25·2	455	2·74

Alcohol as Solvent.

Hexadecyl Alcohol, $C_{16}H_{24}O=242$.

73	61·90	1·39	15·78	2·114	12·1	2·54	276	1·14
		2·80		4·995	24·5	5·82	316	1·30
		4·23		8·25	34·8	9·26	347	1·43
		6·14		13·43	46·7	14·3	365	1·51
		8·43		19·60	56·0	19·5	372	1·54

Benzil, $C_{14}H_{10}O_2=210$.

75	66·85	0·54	19·72	0·893	4·41	0·98	261	1·24
		1·21		2·023	9·50	2·20	261	1·24
		2·57		5·352	21·6	5·61	316	1·505
		4·02		12·42	39·2	12·12	462	2·20
		5·38		20·01	50·9	22·4	544	2·59

Alcohol as Solvent—(continued).

Phenanthrene, $C_{14}H_{10}=178$.

t	*p*	*p* − *p′*	*G*	*g*	Per cent.	100 *n*/*N*+*n*.	*m′*.	*m′*/*m*.
75	66·91	1·10	15·78	1·105	6·70	1·82	198	1·11
		2·15		2·483	13·87	4·01	224	1·26
		3·00		4·399	22·2	6·89	279	1·57
		3·92		7·65	33·1	11·4	368	2·06
75	66·97	0·90	19·72	1·033	5·09	1·36	181	1·016
		1·19		1·462	7·03	1·92	190	1·07
		1·87		2·667	12·12	3·45	222	1·247
		2·75		4·537	19·06	5·71	252	1·42
		3·28		6·54	25·3	8·02	303	1·70
		3·59		8·192	29·8	9·88	344	1·93
		4·03		10·40	35·0	12·20	368	2·17

Azobenzene, $C_{12}H_{10}N_2=182$.

t	*p*	*p* − *p′*	*G*	*g*	Per cent.	100 *n*/*N*+*n*.	*m′*.	*m′*/*m*.
75	67·15	1·26	15·78	1·356	8·09	2·18	212	1·165
		2·36		2·881	15·8	4·52	236	1·30
		3·47		5·029	24·6	7·63	276	1·52
		4·56		8·30	35·0	12·0	342	1·88
		5·70		13·08	46·0	17·8	421	2·31
		6·88		20·60	57·2	25·3	550	2·96
75	67·15	7·35	7·89	12·95	63·2	30·4	647	3·56
		8·90		19·45	72·3	39·6	781	4·29
		10·98		29·84	80·1	50·2	939	5·16
		13·63		45·05	85·9	60·2	1083	5·96

The experiments described in this paper were made in the Chemical Laboratories of the University of Liverpool and the Harris Institute, Preston. The author wishes to express his indebtedness to the late Dr. J. C. Brown for supplying a dividing engine and several chemicals, and to Dr. P. F. Frankland for the loan of the electromagnetic stopcock.

CRICKLEWOOD. [*Received, March 2nd*, 1916.]

XXXVI.—*The State of Potassium Oleate and of Oleic Acid in Solution in Dry Alcohol.*

By MARY EVELYN LAING.

EVER since Krafft's second paper (Krafft, *Ber.*, 1899, **32**, 1584; compare Krafft and Strutz, *Ber.*, 1896, **29**, 1328) on the molecular weights of the salts of the higher fatty acids in dry alcohol, soap has served as the typical instance of a substance which is a crystal-

loid of normal molecular weight in alcohol, although in water it is a colloidal electrolyte.* This conception and definition of colloidal electrolytes to which the six years' study of soap solutions in this laboratory up to 1914 has led, made it appear possible that in alcohol also the apparent simplicity of Krafft's last result was illusory and that, as in some aqueous solutions, extensive dissociation and formation of colloïd might occur, the more so since his previous paper had indicated that in absolute alcohol soap existed in the form of double molecules. For this reason, the molecular weight in alcohol has been redetermined. Further, the electrical conductivity has been measured in order to ascertain whether the ionisation is great or negligible.

Potassium oleate was chosen for study because of its ready solubility in alcohol, since in many cases the formation of colloid or colloidal electrolyte is only appreciable in high concentration. Its solutions are never devoid of opalescence, and they have a distinct tendency to froth.

The result has been to show that potassium oleate both in anhydrous and in moist ethyl alcohol is essentially a simple electrolyte dissociating to a very moderate extent into simple ions. Only quite small amounts of colloid can be present.

Solutions of oleic acid, which also froth readily and for which no ebullioscopic data existed, were likewise investigated, particularly as Dennhardt (*Diss.*, 1898; *Ann. Phys. Chem.*, 1899, [iii], **67**, 325) had obtained conducting curves in methyl and ethyl alcohols, exhibiting in each case a pronounced maximum and minimum. Such phenomena are of very frequent occurrence in the literature of non-aqueous solutions, and in certain cases their explanation appears to me to offer great difficulties.

The results have shown that Dennhardt's data are quite untrustworthy (for other evidence, see below), and that oleic acid also, in all concentrations, is a simple electrolyte, only very slightly dissociated. Consequently, the theoretical difficulties of interpretation vanish, and it seems quite possible that a number of other similar cases may also be due to experimental error.

EXPERIMENTAL.

Dry ethyl alcohol was prepared from absolute alcohol which had been kept over specially burnt quicklime for three years; during

* "Colloidal electrolytes are salts in which one ion has been replaced by a heavily hydrated micelle that conducts electricity just as well or even better and carries an equivalent sum total of electrical charges." (See McBain, *Trans. Faraday Soc.*, 1913, **9**, 99. *Kolloid Zeitsch.*, 1913, **13**, 56; T., 1914, **105**, 957, and McBain and Salmon, *J. Amer. Chem. Soc.*, 1918.

this time, the liquid had become a soft, pale yellow jelly owing to the formation of calcium ethoxide. The alcohol was distilled from this material and preserved with the usual precautions. Three separate specimens were used, and identical results obtained in molecular weight determinations. It had D_4^{15} 0·7925, a value only 0·1 per cent. too low, indicating, presumably, the presence of a small amount of ether (water would affect the density in the opposite direction).

All vessels and instruments were carefully calibrated, and the precautions described in earlier papers from this laboratory observed. The oleic acid used was colourless, almost odourless, melting at 9·0°, and having D_4^{18} 0·8938.

Dry potassium oleate was prepared in the following manner. Potassium balls were cleaned by washing with several changes of methylated ether; the balls were at once wiped with filter paper and dropped into dry alcohol. Finally, oleic acid was added to the potassium ethoxide until a sample diluted with about one-quarter of its weight of water (previously boiled) gave a neutral reaction towards phenolphthalein. The solution was then evaporated under diminished pressure over calcium chloride, the potassium oleate being left as a soft, pure white powder.

Molecular Weight of Potassium Oleate in Anhydrous and Moist Alcohol.

Beckmann's ordinary apparatus was employed. Concentrations are expressed in mols. per 1000 grams of alcohol (weight normality).

Concentration.	Grams per 100 grams of alcohol.	Rise in boiling point.	Molecular weight.
0·14	4·518	0·173°	303·4
0·32	10·21	0·388	302·4
0·44	14·09	0·528	306·7
0·49	15·71	0·590	306·1
0·54	17·34	0·654	305·2
0·63	20·16	0·764	303·2
0·70	22·32	0·820	305·6
0·84	26·91	1·008	306·9
0·91	29·18	1·100	305·2
1·00	32·04	1·238	297·9
1·14	36·80	1·350	311·6
		Mean	304·9
		Theory	320·5

The experiments comprise a number of independent series extending up to fully saturated solution. The results show no tendency for the molecular weight to alter with concentration, and they give data rather smaller than that required for the simple molecular weight. This is explained by the moderate dissociation measured below. The value here obtained agrees substantially

with that which Krafft himself found in his second paper, namely, 347, instead of twice the molecular weight.

On the addition of 1, 2, 3, and 4 per cent. of water to the solution, only a very slight alteration in the molecular magnitude was observed, the soap still having a simple molecular weight instead of the larger numbers, namely, 599 to 670, obtained by Krafft and Strutz in their first paper, which appear to be erroneous (see below).

Only the data for the addition of 3·8 per cent. of water (by weight) to the solvent need be presented.

Concentration.	Grams per 100 grams of alcohol.	Rise in boiling point.	Molecular weight.
0·205	6·697	0·243°	311·9
0·278	8·978	0·330	309·7
0·339	10·86	0·400	311·1
0·463	14·84	0·540	315·7
		Mean ...	311·9
		Theory ...	320·5

Krafft considered that his own experiment had confirmed his earlier work with Strutz, for, on the addition of 1·5 c.c. of water to the boiling alcoholic solution, the boiling point was depressed by 0·09°. He appears to have overlooked the fact that a mixture of alcohol and water, containing 96 per cent. of the former, gives a minimum constant-boiling mixture, and therefore the addition of 4 per cent. of water will lower the boiling point of dry alcohol or any solution made from it by about 0·126°. Krafft's experiment, then, if properly calculated, corroborates that just described, and consequently this earlier work is disproved.

Conductivity of Potassium Oleate in Dry Alcohol.

Closed cells of borosilicate glass were employed. The solutions were either made up in the cell by weighing in the constituents or they were made up *ad hoc* and immediately introduced for measurement.

A preliminary experiment on a nearly saturated solution at 18° gave a molecular conductivity of 1·01 mhos. This solution contained 0·1990 gram of potassium oleate in 16·10 grams of alcohol, and therefore its weight-normality was 0·385N, or nearly 0·3N by volume.

The significance of this result depends on the value of the conductivity, at infinite dilution, in alcohol, which is generally accepted as being one-third of the value in aqueous solution. This leads to a value for α, the degree of ionisation, of 3 per cent.

The solubility increases rapidly on heating, and since it is

impossible to predict the behaviour of non-aqueous solutions on further concentration, the remaining measurements were carried out at 40° and 60°. These are given in table I.

TABLE I.

Conductivity of Potassium Oleate in Ethyl Alcohol at 60°.

Weight normality.	Volume normality.	Density.	Specific conductivity.	Molecular conductivity.
1·14	0·68	0·8220	0·001927	2·806
0·76	0·49	0·8030	0·001812	3·679
0·57	0·38	0·7920	0·001694	4·421
0·46	0·31	0·7850	0·001566	5·045
0·38	0·27	0·7800	0·001452	5·483
0·30	0·22	0·7750	0·001285	5·948
0·23	0·16	0·7705	0·001187	7·053
0·14	0·11	0·7640	0·000891	10·64
0·03	0·02	0·7565	0·000381	19·20

Conductivity at 40°.

0·57	0·39	0·8013	0·001477	3·799
0·46	0·32	0·7961	0·001372	4·359
0·38	0·27	0·7922	0·001291	4·800
0·30	0·22	0·7884	0·001734	5·182
0·23	0·17	0·7848	0·001031	6·160
0·14	0·11	0·7810	0·0008143	7·567
0·03	0·026	0·7755	0·0003420	13·43

The determinations of the densities of the concentrated solutions were not easy, since the solutions frothed readily and on slight cooling solidified in the form of a curd. For these, the arms of the pyknometer were made vertical, with the mark on one just opposite the tip of the other. Around the latter a glass mantle was fitted by means of a loose cork, and the solution was protected from the cork by a thin layer of clean mercury. During the adjustment, this reservoir was raised, so that the open tip of the pyknometer was immersed in the soap solution. As soon as the adjustment to the mark had been made, the reservoir was lowered and emptied, leaving the pyknometer exactly full and completely immersed in the thermostat.

The density is nearly, although not quite, proportional to the concentration. In the case of oleic acid, the divergence from a straight line is slightly greater.

It is seen from the above tables that the conductivity at 60° rises steadily from 2·81 mhos for a 1·14N(weight)-solution up to the fairly large value of 19·2 for a 0·03N(weight)-solution, without exhibiting any irregularities.

Since the conductivity at infinite dilution at 60° probably lies between 50 and 60 mhos., the dissociation evidently rises from a value of about 3 per cent. in N-solution to about 30 per cent. in

0·03N-solution. In every case, then, practically all the soap is in crystalloidal form, although, no doubt, a very small amount of colloid must be present.

Oleic Acid in Dry Alcohol.

Oleic acid is a typical case of a substance giving anomalous data in non-aqueous solution, consequently its molecular weight by the ebullioscopic method was first studied.

The results of several series of determinations may be summarised as follows.

From 0·2898 gram to 6·914 grams of acid were dissolved in 12·96 grams to 13·33 grams of alcohol, giving solutions which were 0·07, 0·08, 0·1, 0·26, 0·3, 0·56, 0·60, 0·80, 0·97, and 1·8N(weight), and from the rise in boiling point the following molecular weights are calculated: 297·2, 283·1, 273·6, 270·5, 284·0, 276·0, 294·2, 298·5, 288·1, and 306·9. Mean, 287·1; Calc., 282·3. Difference, 1·7 per cent. There is therefore no doubt with regard to the simple value for the molecular weight or to its constancy over this very great range of concentration. There is clearly also very little dissociation.

We possess very little or no information with regard to the molecular weight of higher fatty acids in water on account of their insolubility in this medium. In quinoline, however, Gabel (*Diss.*, Magdeburg, 1906) found that stearic acid had simple molecular weight, although sodium stearate and palmitate were shown to be colloids.

The next step was to redetermine the conductivity of oleic acid in alcohol. This was measured only at 60°, and the results are given in table II. Every point was determined several times with

TABLE II.

Conductivity of Oleic Acid in Dry Alcohol at 60°.

Weight normality.	Volume normality.	Density.	Specific conductivity.	Molecular conductivity.	$\mu/\sqrt{v} \times 10^{-4}$.	$\mu/\sqrt{v} \times 10^{-}$. corrected[4]
3·64	1·536	0·8368	$1·57 \times 10^{-6}$	$3·58 \times 10^{-3}$	0·24	0·16
1·81	0·955	0·7961	4·01 ,,	4·20 ,,	1·30	1·14
1·44	0·811	0·7905	5·40 ,,	6·66 ,,	1·90	1·72
0·91	0·564	0·7794	5·52 ,,	9·77 ,,	2·30	2·11
0·75	0·482	0·7761	6·56 ,,	13·59 ,,	3·00	2·76
0·47	0·319	0·7695	5·60 ,,	17·54 ,,	3·13	2·85
0·39	0·268	0·7677	5·21 ,,	19·43 ,,	3·20	2·88
0·33	0·238	0·7656	5·04 ,,	21·65 ,,	3·20	2·90
0·13	0·095	0·7593	4·17 ,,	43·85 ,,	4·30	3·76
0·06	0·044	0·7568	2·42 ,,	55·08 ,,	3·60	2·90
0·115	0·011	0·7542	1·21 ,,	110·8 ,,	3·70	2·15
0·011	0·008	0·7540	1·21 ,,	138·2 ,,	4·08	2·40

independent solutions. Some measurements with intermediate concentrations are omitted, to save space, but they fit in smoothly with those presented here.

It will be noticed that the conductivity is very low, making accurate measurement difficult. It is, however, sufficiently higher than that of alcohol itself ($4{\cdot}9 \times 10^{-7}$ at 60°) to make it unmistakable.

In the second place, in contrast to Dennhardt's data (*loc. cit.*), the conductivity rises steadily on dilution. Dennhardt's measurements appear to be inaccurate, and it may be pointed out that Kahlenberg and Schreiner (*Zeitsch. physikal. Chem.*, 1898, **27**, 552) obtained conductivity data for aqueous solutions of sodium oleate which are twice as great as those determined by Dennhardt. In quoting the latter, Goldschmidt remarks (Ubbelohde and Goldschmidt, "Handbuch der Oele und Fette," 1911, III, 47) that the experimental results appear to be due to some error. Again, Dennhardt's data for aqueous potassium oleate differ in some cases from those of Kurzmann (*Koll. Chem. Beihefte*, 1914, **5**, 427) by as much as 30 mhos.

It is very satisfactory to find that the complicated relationships observed by Dennhardt have no real existence, for it would be difficult to explain them, although other similar cases are to be found in the literature of non-aqueous solutions. The point is that they appeared to occur in a substance of simple molecular weight and in regions of extremely low concentration of ions. Thus a mere trace of ion would have to possess a quite impossibly great intrinsic dissociating power, enormously greater even than the sufficiently improbable value ascribed to ionised potassium chloride by Walden (dielectric constant calculated as 14,000). The other alternative would have to be that the ions possessed great tendency towards complex-formation, even in extreme dilution, without, however, an appreciable proportion of the corresponding undissociated complex being formed, even in very concentrated solutions.

Godlewski (*Bull. Acad. Sci. Cracow*, 1904, **6**, 239) found that eight organic acids exhibited in alcohol conductivities of the same order of magnitude as that described above for oleic acid. Further, these acids obeyed the law of mass action. When the ionisation is so small, the law of mass action requires that $\mu / \sqrt{v}$ should be a constant, where μ is the molecular conductivity and v the dilution in litres.

In table II, the penultimate column contains the values of this expression $\mu / \sqrt{v}$, and the last column the same expression corrected for the conductivity of the alcohol. In both cases it is quite

definitely shown that the values are not constant for solutions of greater concentration than $N/8$ or $N/2$ respectively, but both expressions are appreciably constant for the more dilute solutions. The uncorrected values must ultimately continue to rise almost in proportion to the dilution, owing to the fact that the specific conductivity is to be very largely ascribed to the alcohol.

The corrected values are constant, for the fifty-fold range of dilution below $N/2$, within the experimental error, which is, however, necessarily rather large. In other words, the law of mass action applies to these results. The conductivity of the highest concentrations diminishes rapidly, obviously because the solvent is being altered from alcohol to a mixture in which oleic acid actually preponderates.

Wightman, Lloyd, Wiesel, and Jones (*J. Amer. Chem. Soc.*, 1914, **36**, 2243; 1916, **38**, 121) have measured the conductivity of more than forty organic acids in alcohol, including a few of those measured by Godlewski, and find a conductivity of the same magnitude, but the conductivity does not obey the law of mass. Their results, like Wilderman's (*Zeitsch. physikal. Chem.*, 1894, **14**, 231, 247), tend to increase almost as fast as the dilution, instead of being proportional to the square root of the dilution. This deviation from the law of mass action is consequently in the opposite direction from that observed for strong electrolytes in aqueous solution.

It appears possible that Jones's data were not corrected for the conductivity of the alcohol, although in $N/512$-solution this amounted to more than two-thirds of the conductivity. Their results in some cases obey the law of mass action if corrected, some are erratic, a few diminish rapidly, whilst half still rise with dilution.

It is really not surprising that the law of mass action is not always observed, as the relationships are complicated by the esterification which slowly takes place. This must remove hydroxyl ions formed by the alcohol and enhance the amount of ethyl ions present.

The slow esterification does not alter the conductivity much, in spite of the water formed. A $3{\cdot}4N$(weight)-solution does not alter in conductivity at 60° by more than 1 or 2 per cent. in six hours from the time of preparation. According to Jones and his coworkers, a certain amount of esterification must occur, although they found the rate to be independent of the temperature within their experimental error. Dennhardt (*loc. cit.*) found in an 18·4 per cent. solution of oleic acid in methyl alcohol an increase of only 2·9 per cent. in fifteen hours at 25°, and an increase of

4 per cent. in a 36 per cent. solution in fifteen hours. In an 18·5 per cent. solution in ethyl alcohol he observed an increase of 0·2 per cent., and in a 53 per cent. solution an increase of 2·6 per cent. in specific conductivity.

Although in a given time the proportion of acid converted into ester and water would be about the same for any one temperature, independent of the concentration; on diluting there is now more than one substance present, of which the dissociation, and therefore the conductivity, is increasing with dilution. This would seem to explain the general nature of the results, but a study of the esters in alcoholic solution and further knowledge of the part the ions play in the mechanism of the reaction are required for a full discussion of the phenomena.

No stress can be laid on the confirmation of the law of mass action by some acids in alcoholic solution, since all such systems are either in process of reaction or have attained equilibrium through the presence of a large amount of ester.

Mixtures of Oleic Acid and Potassium Oleate in Alcohol.

There is a slight but distinct tendency for oleic acid and potassium oleate to unite, with the formation of a complex. This is shown by the following ebullioscopic data for mixed solutions, where the concentration of the oleate was $0·16N$(weight) and that of the oleic acid varied from $0·27N$ to $0·57N$. The molecular weights found were 311·9, 289·1, 296·4, 322·8. Mean, 305·0; Calc., 282·3. Difference, 7·4 per cent. Found above (p. 440), for pure oleic acid solutions, 287·1.

The conductivity of potassium oleate in alcohol is diminished by the addition of oleic acid to the solution. For instance, $0·28N$(weight)-solution of potassium oleate at 60° possessed a specific conductivity of 0·001552; on adding 2·88 equivalents of oleic acid [$2·88 \times 0·28N$(weight)], the specific conductivity was lowered by 44·3 per cent. to 0·000865. A $0·34N$(weight)-solution of the oleate exhibiting a conductivity of 0·001381 on addition of 0·164 equivalent ($0·164 \times 0·34N$) of oleic acid gave the value 0·001336, a lowering of 3·3 per cent. Although the lowering is thus proportional to the oleic acid added, the effect is not simply dilution of the solution by indifferent oleic acid, since in the first case the weight of oleic acid was only 21 per cent. of the total weight of solution. This shows again that a certain amount of a complex is formed.

Summary.

In moist as well as in dry alcohol, potassium oleate is a typical simple electrolyte moderately dissociated. Oleic acid, contrary to previous data, is also a normal electrolyte exceedingly little dissociated, but apparently obeying the law of mass action on dilution. In mixtures of oleic acid with potassium oleate, a small amount of a complex compound is formed, which tends to show that a small proportion of the ions of the oleic acid itself are also complex. This trace probably accounts for the slight but distinct tendency of all these solutions towards opalescence and frothing.

My thanks are due to Dr. J. W. McBain, at whose suggestion this work was carried out, and also to the University Colston Society for a grant which has defrayed the expenses of this investigation.

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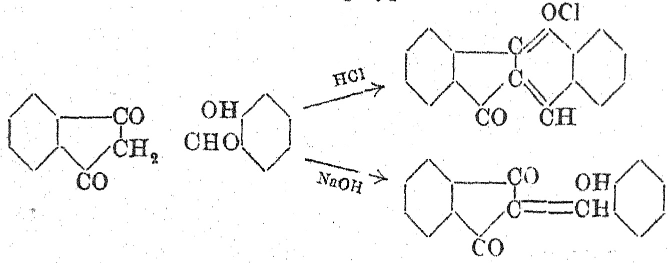
XXXVII.—*Synthesis of Pyranol Derivatives.*

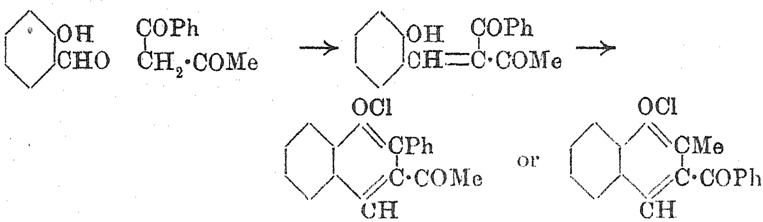
By SARAT CHANDRA CHATTERJI and BROJENDRA NATH GHOSH.

IT has been shown by one of us (T., 1915, **107**, 1442) that diketohydrindene condenses with *o*-hydroxyaldehydes, giving ketoindopyranol derivatives of the following type:



It is apparent that the existence of the $\cdot CO\cdot CH_2\cdot CO\cdot$ group in diketohydrindene is responsible for these changes, and in order to show that the reaction is a general one, we have extended the investigation to other substances containing this group. In the present paper, we describe experiments with benzoylacetone and acetylacetone. One would expect that in these cases also the

interaction between, say, benzoylacetone and salicylaldehyde would proceed in the normal way, yielding condensation products of the following type:



(I.) (II.)

The reaction is not, however, so simple as that indicated by the above equations. Under different conditions, we have been able to isolate three different products from the condensation of these two substances. Two are actually the same as I and II, one being soluble in alcohol and the other insoluble. The former loses hydrogen chloride very readily on exposure to air, and is converted into its base. From its similarity to acetylacetone, we are of opinion that it may have the constitution indicated by I, the insoluble substance having the constitution II. The third product is a complex substance resulting from the reaction of one molecular proportion of salicylaldehyde with two molecular proportions of benzoylacetone, the constitution of which has not yet been determined.

In the case of acetylacetone and salicylaldehyde, two different substances were isolated, one of which was soluble and the other insoluble in acetic acid. In this reaction, the intermediate unsaturated ketone could not be isolated.

In the case of benzoylacetone and salicylaldehyde, the intermediate *salicylidenebenzoylacetone* was obtained by boiling the insoluble compound, formed by their condensation in the presence of hydrogen chloride, with excess of aqueous potassium hydroxide (50 per cent.). The substance, on being boiled with dilute hydrochloric acid, condenses again to the original anhydrohydrochloride (I or II).

The acetyl or benzoyl groups of these substances are very stable, as they are not eliminated on boiling with dilute hydrochloric acid for a long time or even with sodium hydroxide solution.

The bases corresponding with both I and II have also been isolated, their constitutions being represented by the same formulæ except that chlorine is replaced by hydroxyl.

Experimental.

Preparation of Benzoylacetone.

Claisen (*Ber.*, 1887, **20**, 655) prepared this compound by treating a mixture of acetone and ethyl benzoate with alcohol-free sodium ethoxide, but the authors have found the following method much more easy and advantageous.

A mixture of 30 grams of ethyl benzoate and 15 grams of acetone was treated with 50 c.c. of dry ether, and then 4·6 grams of sodium wire or shavings were added. The whole was cooled in water, and the sodium salt at once began to separate. After an hour, the mixture was gently warmed on a water-bath for a few minutes. The precipitate was collected, washed with ether, and then spread on a porous plate. The dried sodium salt was dissolved in a small quantity of hot water, and the cooled solution quickly acidified with dilute sulphuric or acetic acid. The precipitate was collected and washed, and was found to consist of almost pure benzoylacetone.

Condensation of Benzoylacetone and Salicylaldehyde.

Benzoylacetone (6·4 grams) and salicylaldehyde (2·4 grams) were dissolved in the minimum quantity of methyl alcohol, and a current of dry hydrogen chloride was passed through the solution for two hours. The mixture became hot and assumed a dark red colour, but no solid substance separated. After about five hours, the liquid was poured into dilute hydrochloric acid, when a dark green substance separated. This was collected, washed with dilute hydrochloric acid, and finally recrystallised from alcohol containing dilute hydrochloric acid:

0·1389 gave 0·4125 CO_2 and 0·0667 H_2O. C=80·9; H=5·3.

$C_{27}H_{20}O_3,\frac{1}{2}H_2O$ requires C=80·8; H=5·3 per cent.

The compound crystallises in dark green needles which melt at about 120°. It dissolves in acetic acid, yielding a green solution exhibiting a slight green fluorescence. On boiling with hydrochloric acid, the substance remains unchanged. It forms a very unstable hydrochloride which evolves hydrogen chloride on being kept in a desiccator.

3-*Acetyl*-2-*phenyl*-1:4-*benzopyranol Anhydrohydrochloride* (I) or 3-*Benzoyl*-2-*methyl*-1:4-*benzopyranol Anhydrohydrochloride* (II).

A mixture of 3·2 grams of benzoylacetone and 2·4 grams of salicylaldehyde was dissolved in excess of methyl alcohol, and the

solution cooled in a freezing mixture. A slow current of dry hydrogen chloride was then passed into it, care being taken that no rise of temperature occurred during the reaction. The solution gradually darkened in colour, and a dark red, crystalline substance separated. The mixture was then poured into dilute hydrochloric acid, and the dark, crystalline substance which was obtained in this way was collected and washed with dilute hydrochloric acid. On attempting to recrystallise it from alcohol, it was found that only a small portion of it (*B*) was soluble in alcohol, whereas the bulk of the precipitate (*A*) was insoluble in practically all the ordinary solvents. The substance *A* was kept in a desiccator over potassium hydroxide and analysed:

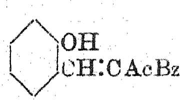
0·1793 gave 0·4594 CO_2 and 0·0807 H_2O. C=69·8; H=5·0.
0·2646 „ 0·1259 AgCl. Cl=11·8.
$C_{17}H_{13}O_2Cl,\frac{1}{2}H_2O$ requires C=69·6; H=4·8; Cl=12·1 per cent.

It is a black, crystalline substance which does not melt. It dissolves in concentrated sulphuric acid, forming a red solution which does not show any fluorescence.

The *base* corresponding with the salt (*A*) was prepared by triturating about 1 gram with an excess of a 2 per cent. solution of sodium hydroxide. After keeping the mixture for about half an hour, it was filtered and the residue washed until the filtrate was free from alkali. The substance was then kept in a desiccator over sulphuric acid:

0·1779 gave 0·4679 CO_2 and 0·0916 H_2O. C=71·7; H=5·7.
$C_{17}H_{14}O_3,H_2O$ requires C=71·8; H=5·6 per cent.

The base is a pale brown substance which is insoluble in all the ordinary solvents. On heating, it does not melt, but chars. It is reconverted into the original salt on being treated with dilute hydrochloric acid.

Salicylidenebenzoylacetone, 

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This was prepared by heating the insoluble pyranol anhydrohydrochloride with a 50 per cent. solution of potassium hydroxide for several hours. After being cooled, the mixture was acidified with dilute hydrochloric acid, filtered, and the residue washed with hot water. It is a pale brown substance which does not melt on heating, and changes to a chocolate colour on exposure to air:

0·1865 gave 0·5066 CO_2 and 0·0990 H_2O. C=74·0; H=5·8.
$C_{17}H_{14}O_3,\frac{1}{2}H_2O$ requires C=74·1; H=5·4 per cent.

Attempts to prepare this substance directly by condensing the

constituents in the presence of piperidine or methyl-alcoholic sodium hydroxide were unsuccessful. In every case, a gummy material separated from which no definite substance could be isolated.

Substance B.—As this was formed in very small amount, we isolated it by condensing molecular quantities of benzoylacetone and salicylaldehyde in excess of methyl alcohol and filtering off the precipitate formed. The alcoholic solution was then mixed with dilute hydrochloric acid, when a brown substance separated, which was collected, washed, redissolved in alcohol, and reprecipitated with dilute hydrochloric acid:

0·1815 gave 0·4757 CO_2 and 0·0813 H_2O. C=71·4; H=4·9.

$C_{17}H_{13}O_2Cl$ requires C=71·8; H=4·6 per cent.

This pyranol derivative is a pale brown substance which fuses at a high temperature. On keeping it exposed to the moist atmosphere, it slowly hydrolyses, giving off hydrogen chloride, and being converted into the corresponding base.

The *base* was prepared by dissolving the corresponding anhydrohydrochloride in alcohol and treating the solution with an excess of aqueous sodium acetate. The precipitate was collected, washed with water, and then crystallised from dilute alcohol, when it separated in green prisms, which appeared grey when dry:

0·1426 gave 0·3744 CO_2 and 0·073 H_2O. C=71·6; H=5·7.

$C_{17}H_{14}O_3,H_2O$ requires C=71·8; H=5·6 per cent.

Condensation of Acetylacetone and Salicylaldehyde.

This condensation product was prepared by dissolving 2 grams of acetylacetone and 2·5 grams of salicylaldehyde in the minimum quantity of methyl alcohol, and then saturating the solution with a rapid stream of dry hydrogen chloride for three hours, care being taken to avoid any rise in temperature. The mixture gradually became dark red and soon deposited crystals. The whole was poured into dilute hydrochloric acid, and the substance was collected, washed, and dried. On boiling with acetic acid, it was found that a large portion of it dissolved, but a small quantity remained insoluble although boiled with much acetic acid. The soluble portion was reprecipitated with dilute hydrochloric acid and kept in a vacuum desiccator:

0·2007 gave 0·5617 CO_2 and 0·1009 H_2O. C=76·3; H=5·58.

$C_{17}H_{16}O_3$ requires C=76·1; H=5·9 per cent.

It crystallises in violet-coloured prisms, which do not melt but carbonise on heating. It forms a hydrochloride which, on keeping, gradually loses hydrogen chloride and becomes quite free from

the acid after two or three days. It is soluble in pyridine and other solvents of high boiling point.

The *phenylhydrazone* of this substance was prepared by dissolving 1 gram in glacial acetic acid and boiling the solution with an excess of phenylhydrazine for about half an hour. The mixture, after being cooled, was poured into dilute acetic acid, and the precipitate collected, washed, and recrystallised from alcohol, separating in rose-red needles which melt at a high temperature—above 300°:

0·1431 gave 10 c.c. N_2 at 29° and 756 mm. N = 7·9.
$C_{23}H_{22}O_2N_2$ requires N = 7·8 per cent.

The portion insoluble in acetic acid was kept in a vacuum desiccator over sulphuric acid for several days and then analysed. It was a chocolate-coloured substance which did not melt:

0·1251 gave 0·3383 CO_2 and 0·0605 H_2O. C = 73·7; H = 5·3.
$C_{24}H_{22}O_5$ requires C = 73·8; H = 5·6 per cent.

Our thanks are due to Principal F. W. Südmersen for the kind interest he has taken in the work, and also to the Research Fund Committee for grants which have defrayed the cost of some of the materials used in the work.

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GAUHATI, ASSAM. [*Received, December 17th*, 1917.]

XXXVIII.—*The Abnormality of Strong Electrolytes. Part I. Electrical Conductivity of Aqueous Salt Solutions.*

By JNANENDRA CHANDRA GHOSH.

VAN'T HOFF discovered that aqueous solutions of electrolytes show an abnormal osmotic pressure. For such solutions, as is well known, the equation $PV = iRT$ holds good. Arrhenius suggested that $i = (1 - a) + na$, where a is the degree of dissociation and n the number of ions into which a molecule dissociates. According to Arrhenius, there is, therefore, an equilibrium between ions and undissociated molecules in solution. Ostwald attempted to apply the law of mass action to this case of chemical equilibrium, but his dilution law, $\frac{a^2}{(1-a)V} = K$ fails absolutely in the case of strong

electrolytes. Various hypotheses have been put forward to explain this anomaly, for example, hydration of ions, change in ionic friction with dilution, formation of complexes, action of salts, change in the dielectric constant of the solvent, interaction between molecules and ions, etc. None, however, has been found to be satisfactory. It appears to the present author that the fundamental suggestion of Arrhenius, postulating the co-existence of undissociated molecules and ions in solution, is probably not valid. The question of chemical equilibrium does not enter into the question at all in the case of strong electrolytes. In solutions of strong electrolytes only ions are present, and the attractive forces between ions are only governed by the physical laws of electrostatic attraction. On the basis of this simple assumption, a quantitative interpretation of the increase of molecular conductivity with dilution will be given.

Number of Free Ions in a Solution containing a Gram-molecule of Salt from the Classical Kinetic Theory.—According to a well-known theorem of the kinetic theory of gases, there is a simple relation between the total number of molecules and the number which can perform the work required to displace a molecule from the sphere of mutual attraction. In applying this theorem to calculate the number of free ions in a solution containing a gram-molecule of salt, we may proceed thus:—A salt solution, where only ions are present, is perfectly analogous to a gaseous system. The electrical attraction between the oppositely charged ions corresponds with the molecular forces in an imperfect gas. Due to this attraction, a field of force exists in the interior of a salt solution, the potential of which may be represented by A, that is, A is the work done when the ions constituting a gram-molecule go beyond one another's sphere of attraction. The ions in a solution are, of course, endowed with a kinetic energy of translation, the distribution of velocities being governed by Maxwell's law. As the work done in escaping from the electrical field inside the solution must be derived from the kinetic energy of the ions, only those ions can escape which have a kinetic energy greater than the work to be done. The problem before us is, therefore, to determine what fraction of the total number of ions has a velocity greater than the critical velocity v_0, where $\frac{1}{2}mv_0^2=\frac{A}{nN}$. Here N is Avogadro's number ($6{\cdot}16\times10^{23}$ Millikan's value), n the number of ions into which a molecule dissociates, and $\frac{A}{nN}$ is therefore the work to be done by each ion before it can escape. Now if V' is the most probable speed of an ion, then the fraction we are considering is

represented by $e^{-v_0^2/V'^2}$ where e is the base of natural logarithm. Now if c is the square root of the mean of the squares of the speeds, we have $c^2 = \frac{3}{2}V'^2$, and the required fraction becomes

$$e^{-\frac{3}{2}v_0^2/\frac{3}{2}c^2} = e^{-\frac{1}{2}n.N.mv_0^2/\frac{1}{2}nN.mc^2} = e^{-\frac{A}{nRT}}.$$

(Since there are ions of different equivalent weights in the solution, m signifies the mean mass of an ion.)

As nN is the total number of ions, the number of free ions

$$= nNe^{-\frac{A}{nRT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Conductivity of Salt Solutions.—It is well known that Ohm's law holds good for electrolytic conduction. No energy is therefore lost in overcoming the forces of mutual attraction between ions. Any hypothesis put forward to explain the phenomenon of electrolytic conduction must take into consideration this fundamental fact. According to Arrhenius, the molecular conductivity of a salt solution at infinite dilution is at a maximum, because there the salt is entirely dissociated into ions. With diminishing dilution the molecular conductivity diminishes, because the salt is only partly dissociated and hence the number of ions is less. On the hypothesis that in aqueous solutions we have only ions present subject to forces of electrical attraction, a neat explanation can also be given. Since during electrolytic conduction no energy is lost in overcoming the forces of electrical attraction, only those ions take part in the conduction of electricity which by virtue of their kinetic energy can overcome the forces of mutual attraction. These are also the ions which can be liberated on the electrode surface. The rest are inactive so far as electrical conduction is concerned. At any dilution, the number of free conducting ions is equal to

$$n.N.e^{-\frac{A}{nRT}}$$

where A is the work at that dilution. The molecular conductivity is proportional to this number. At infinite dilution A is zero, since the ions are outside one another's sphere of attraction, and therefore the number of conducting ions is nN. Therefore

$$\frac{\mu_v}{\mu_\infty} = \frac{nNe^{-\frac{A}{nRT}}}{nN} = e^{-\frac{A}{nRT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$A = nRT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

The Electrical Work Necessary to Separate the Component Ions of a Gram-molecule at Various Dilutions.

(a) *The Arrangement of Ions in Solution.*—In the interior of a solution, the electrical forces between ions are balanced. In order that this equilibrium condition may be attained, the ions should arrange themselves in a definite fashion. It is necessary that they should adopt a geometrical disposition of perfect regularity, as do the atoms when they assume a crystalline structure, under the forces of mutual attraction. This does not necessarily mean that the ions in solution are devoid of any kinetic energy whatsoever. What we assume here is that the mean disposition of the oppositely charged ions should conform to some patterns in space. According to Ostwald, the conditions of the salt molecule in the crystalline state is not far removed from the state of solution. Indeed, there is not much difference between a crystalline salt and the same in a molten condition as regards their electrochemical properties. Thus, the experiments of Graetz (*Ann. Phys. Chem.*, 1890, [iii], **40**, 18) have shown that there is no sudden change in electrical conductivity as we pass from the solid to the fused state.

It may well be that even the forces which group the atoms of a solid salt according to a definite space-lattice are electrical in nature. In the first place, therefore, we make the perfectly reasonable assumption that the marshalling of the ions of a salt in a state of solution is analogous to the arrangement of its atoms in the crystalline structure.

(b) *The Forces of Electrical Attraction between Ions.*—For the calculation of the electrical work it is necessary to make another assumption. In solution, an ion takes up a definite mean position because of the forces of electrical attraction exerted by oppositely charged ions surrounding it.

We may, however, suppose that the component ions of a salt-molecule form a completely saturated electrical doublet. When a univalent ion tends to pass out of solution, the solution becomes electrified with an opposite unit charge and attracts it as a whole. By assuming the existence of electrical doublets we only locate the centre of attraction inside the solution. The work necessary for separating the component ions of a molecule is the electrical work done in moving the ions constituting a doublet from their fixed mean distance in the solution to an infinite distance apart. Thus for an aqueous solution of a binary salt like potassium

chloride, the electrical work necessary for separating the potassium and chlorine ions

$$= \frac{E^2}{Dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where E is the charge on each ion, D the dielectric constant of water, and r the distance between the oppositely charged ions at that dilution.

For salts of the type of barium chloride, there are two electrical doublets associated with each molecule, Cl–Ba–Cl. Now let us remove the two chlorine ions successively from the sphere of influence of the barium ion. For the first chlorine ion, the electrical work is $\frac{E^2}{D.r}$, the same as is necessary for separating the components of a doublet in potassium chloride solutions. The removal of the second chlorine ion is much more difficult. This ion is attracted by two opposite charges, and hence the work due to electrical attraction is $\frac{2E^2}{D.r}$. The work necessary for separating the component ions of a molecule of barium chloride is therefore

$$\frac{3E^2}{D.r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For salts of the type of magnesium sulphate the electrical work is

$$\frac{4E^2}{D.r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

for each ion here carries two unit charges. Now, if we can determine the value of r for these types of salt at various dilutions, A is known, and therefore the ratio $\frac{\mu_v}{\mu_\infty}$, which is equal to $e^{-\frac{A}{nRT}}$ can at once be calculated.

(c) *Calculation of the Distance between Ions in Solutions of Binary Salts.*—The distance between the oppositely charged ions in an aqueous solution can be very simply determined on the assumption previously made. Take, for example, the case of potassium chloride. Bragg has actually measured the distance between the planes 100, 110, 111 of this cubic crystal, and has found that it is the simple cubic lattice to which the arrangement of the atoms conforms. We therefore expect that in solutions, also, the sets of points corresponding with the mean position of the ions form a cubic space-lattice. It is obvious that in a cubic lattice there is only one point, that is, one ion, associated with a unit cell, the distance between the oppositely charged ions being

the linear dimension of the unit cell. Since there are $2N$-ions, the total volume occupied by $2N$-unit cubes $=2N \cdot r^3 = V$ (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}} \text{ and } A = \frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} \quad . \quad . \quad (6)$$

$$= 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $E = 4{\cdot}7 \times 10^{-10}$[E.S.U.] and $D = 81$ at 18°.

For salts like ammonium chloride or potassium nitrate, where complex univalent radicles are encountered, we are also justified in assuming that the distance between ions at equivalent dilutions is approximately the same as in the case of potassium chloride solutions.

(d) *Calculation of the Distance between Ions in Solutions of Salts like Barium Chloride.*—Crystals of calcium fluoride, the constitution of which is perfectly analogous to that of barium chloride, have been thoroughly investigated by Bragg (*Proc. Roy. Soc.*, 1914, A, **89**, 474). In a fluorspar crystal, the calcium atoms are arranged in a face-centred cube lattice, whilst the fluorine atoms occupy the centres of the small cubes. This structure explains how, for each calcium atom, two fluorine atoms may be arranged to form a cubic lattice. Assuming that the arrangement of the barium and chlorine ions in solution corresponds with the fluorspar lattice, we find that each unit cube of the lattice is associated with half an ion of barium. If r be the linear dimension of the unit cube, since there are N-barium ions, $2N \cdot r^3 = V$ (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}}.$$

The chlorine ions, from analogy, should occupy the centres of unit cubes, hence the distance between the barium ion and the chlorine is $\frac{\sqrt{3}}{2} r$. Therefore the electrical work required to separate the components of a gram-molecule is equal to

$$\frac{3NE^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} \text{ ergs}$$

$$= 3RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

(e) *Calculation of the Distance between Ions in Solutions of Salts like Magnesium Sulphate.*—No definite structure has yet been assigned to crystals of magnesium sulphate. The fundamental lattice is, of course, not cubic, but a rhombohedron.

It is possible that, owing to the forces of electrical attraction being greater, the oppositely charged ions constituting a doublet should come together as close as possible. Since, however, we are dealing with a salt, the valency volumes of the ions of which are, according to Barlow and Pope's theory, twice as great as that of a univalent ion, the distance between the doublets should be greater than that in the case of potassium chloride. In solution we may take the cube as the fundamental lattice, without introducing any serious error. The above conditions are satisfied if we imagine that the unit cube is formed only by two oppositely charged ions placed at the adjacent corners. The unit cell becomes thus associated with only one-fourth of an ion, as in the cube-centred lattice. If r be the linear dimension of the unit cube at dilution V, then $8N.r^3=V$ (c.c. containing a gram-molecule) or $r=\sqrt[3]{\frac{V}{8N}}$.

r is also the distance between the component ions of a doublet. Therefore the electrical work

$$A=\frac{4.N.E^2\sqrt[3]{8N}}{D\sqrt[3]{V}}=2RT\log_e\frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad (9)$$

From the equations (7), (8), and (9), which contain no unknown quantities whatever, $\frac{\mu_v}{\mu_\infty}$ can be at once calculated for any dilution. In the following tables it will be shown how the observed values of μ_v at 18° agree with those calculated from the above equations. The value of μ_∞ cannot be determined experimentally, but is generally obtained by extrapolation. In the tables, the value of μ_∞ has been calculated from the observed values of μ_v for $0{\cdot}01N$-solutions, and this theoretical value of μ_∞ has then been utilised in calculating μ_v at other dilutions. The observed values of $\mu_v . \times \mu_v$ are from the tables of Kohlrausch and co-workers.

TABLE I.

V = Dilution in litres.

Salt.	μ_∞ calc. from μ_{100}		v = 10.	20.	100.	1000.	5000.
KCl	132·2	μ_v calc.	111·7	115·7	122·5	127·7	129·2
		μ_v obs.	112·0	115·9	122·5	127·6	129·1
NaCl	110·3	μ_v calc.	93·1	96·5	102·0	106·4	108·0
		μ_v obs.	92·0	95·7	102·0	106·5	107·8
LiCl	99·6	μ_v calc.	84·0	87·1	92·1	96·2	97·5
		μ_v obs.	82·4	86·1	92·1	96·5	97·8
CsCl	135·4	μ_v calc.	114·3	—	125·2	130·6	132·5
		μ_v obs.	113·6	—	125·2	130·6	132·0

TABLE I.—(*continued*).

V = Dilution in litres.

Salt.	μ_∞ calc. from μ_{100}		v = 10.	20.	100.	1000.	5000.
NH_4Cl ...	132·0	μ_v calc.	111·3	115·4	122·1	127·4	129·3
		μ_v obs.	110·7	115·2	122·1	127·3	128·8
KBr	134·5	μ_v calc.	113·6	117·7	124·4	129·7	131·7
		μ_v obs.	114·2	117·8	124·4	129·4	130·9
KI	133·5	μ_v calc.	112·7	116·7	123·4	128·7	130·6
		μ_v obs.	113·9	117·2	123·4	128·2	129·5
KNO_3 ...	127·9	μ_v calc.	107·8	111·2	118·1	123·3	124·8
		μ_v obs.	105·0	110·0	118·1	122·9	124·3
$NaNO_3$ ...	105·0	μ_v calc.	88·5	91·8	97·1	101·3	102·8
		μ_v obs.	87·4	91·4	97·1	101·8	103·3
$C_2H_3O_2K$	101·6	μ_v calc.	85·9	88·9	94·0	98·1	99·6
		μ_v obs.	84·0	87·7	94·0	98·3	99·6

The agreement is remarkably good. The difference between the observed and the calculated values is rarely greater than 1 per cent.

TABLE II.

V = Equivalent dilution in litres.

μ_v and μ_∞ are equivalent conductivities.

Salt.	μ_∞ calc. from μ_{100}		v = 10.	20.	100.	1000.	5000.
$BaCl_2$	124·3	μ_v calc.	92·0	97·3	107·7	116·2	119·5
		μ_v obs.	92·2	96·8	107·7	116·9	119·8
$SrCl_2$	121·6	μ_v calc.	89·3	95·2	105·4	113·8	116·9
		μ_v obs.	90·2	94·4	105·4	114·5	117·5
$CaCl_2$	119·1	μ_v calc.	87·5	93·2	103·2	111·4	114·6
		μ_v obs.	87·9	92·8	103·2	111·5	114·4

The difference between the theoretical and the observed values is never greater than 1 per cent.

TABLE III.

V = Equivalent dilution in litres.

μ_v is equivalent conductivity.

Salt.	μ_∞ calc. from μ_{100}		v = 10.	20.	100.	1000.
$MgSO_4$	114·7	μ_v calc.	48·1	57·6	76·6	95·1
		μ_v obs.	50·1	57·0	76·6	100·2
$ZnSO_4$	110·0	μ_v calc.	46·0	55·1	73·4	91·0
		μ_v obs.	46·2	53·5	73·4	98·0
$CuSO_4$	108·0	μ_v calc.	45·2	53·0	72·2	89·6
		μ_v obs.	45·0	51·4	72·2	101·6

At $V=100$ the discrepancy is very large. Below $V=100$ the agreement is quite good. At high dilutions the conductivity is much greater than the calculated value, because of the undoubted hydrolysis of the salts—the interaction between ions and water molecules.

The Temperature-coefficient of the Ratio $\frac{\mu_v}{\mu_\infty}$.—We have seen how the observed values of μ_v agree with those calculated from the equations (7), (8), and (9). There is every reason to believe that the laws of electrical attraction are independent of temperature. The equations, which yield very satisfactory results at 18°, should also hold good at higher temperatures. In our equation for binary electrolytes,

$$A = \frac{N \, . \, E^2 \, . \sqrt[3]{2N}}{D \, . \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v}$$

if the variation of the dielectric constant of water with temperature be known, $\frac{\mu_v}{\mu_\infty}$, can be easily calculated for any temperature. According to Drude, the variation of the dielectric constant of water with temperature between 0° and 76° is given by the following formula:

$$D_t = D_{18}\{1 - 0{\cdot}00436(t-18) + 0{\cdot}0000117(t-18)^2\}.$$

Assuming that this formula holds good up to 100°, the dielectric constant of water at 100° = 52·6. Table IV shows how the calculated values of $\frac{\mu_v}{\mu_\infty}$, at various temperatures agree with the observed data of Noyes and Coolidge (*Zeitsch. physikal. Chem.*, 1903, **46**, 323).

TABLE IV.

Salt.	T°.		v = 12·5.	= 100.
KCl.	18°	$\frac{\mu_v}{\mu_\infty}$ calc.	85·4 per cent.	93·0 per cent.
		$\frac{\mu_v}{\mu_\infty}$ obs.	87·0 ,,	94·0 ,,
	100°	$\frac{\mu_v}{\mu_\infty}$ calc.	82·6 ,,	90·9 ,,
		$\frac{\eta_v}{\mu_\infty}$ obs.	82·6 ,,	91·1 ,,

The coincidence is remarkable. The diminution of the ratio $\frac{\mu_v}{\mu_\infty}$ with increase in temperature may thus be quantitatively explained.

In conclusion, reference should be made to one important point, namely, the question of weak electrolytes. They are invariably either acids or bases. The abnormally high conductivity of hydrogen and hydroxyl ions leaves no room for doubt that here there is a chemical interaction between solvent and solute molecules. Ostwald's dissociation constant is probably related in some way to the constant of these specific chemical reactions.

I take this opportunity of offering my best thanks to Mr. J. N. Mukherjee, M.Sc., for many valuable suggestions. My best thanks are also due to Prof. P. C. Rây.

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XXXIX.—*Spinacene and some of its Derivatives.*

By A. Chaston Chapman.

In a recent communication (T., 1917, **111**, 56) describing the preparation and properties of spinacene and of some of its derivatives, I directed attention to the fact that the formula for the hydrocarbon based on the analysis of the hexahydrochloride (which was the most crystalline and best defined compound I had succeeded in obtaining) was not in good agreement with the results for the determination of the molecular weight by the cryoscopic method. This discrepancy I was unable to explain, and I therefore determined to prepare a further and larger quantity of the hydrocarbon and also of the hydrochloride. I was fortunately able to obtain some more of the shark-liver oil, and proceeded to prepare spinacene from it by the method previously adopted. As in my earlier work, the main fraction boiled within a range of a few degrees and contained only about 0·5 per cent. of oxygen.

As I had reason to believe that metallic sodium was without action on the hydrocarbon, I proceeded to distil it with the addition of some sodium for the purpose of obtaining a product free from oxygen. In my earlier work, only about 50 c.c. of the oil had been distilled in this manner, and then under a pressure of 10 mm. In the present case, a much larger volume of the oil was employed, and owing to the faulty working of the pump, the pressure during distillation remained constant at about 45 mm.,

the bulk of the oil distilling under that pressure at about 290°. It was noticed that during the distillation the liquid in the flask became increasingly dark in colour, and towards the end had become converted into an almost black, tarry mass.

The portion of the oil, which had distilled over between 280° and 295°, was then submitted to fractional distillation (without sodium) at a pressure varying from 35 to 40 mm., and it was found that the boiling point rose gradually from 84° to 298°.

From this result, it is evident that in the presence of sodium and under the conditions above mentioned, spinacene undergoes some decomposition, and that this method cannot consequently be adopted for its purification. I therefore decided to prepare some more of the spinacene by fractional distillation without the use of sodium and at a pressure not exceeding 10 mm. In these circumstances, a large specimen of the hydrocarbon was obtained having the following properties:

Boiling point	260° (corr.)/9 mm.
Specific gravity (15°/15°)	0·8610
Refractive index at 20°..............	1·4956

When examined by the Wijs method, it was found that 100 parts of the hydrocarbon united with 367·9 parts of iodine.

The following molecular weight determinations were made by the cryoscopic method:

I. 0·2262 in 16·83 benzene gave $\Delta^t = -0{\cdot}167°$. M.W. = 394.
II. 0·2371 in 17·07 benzene gave $\Delta^t = -0{\cdot}174°$. M.W. = 391.

This number is higher than that given in my previous paper, and in view of the results obtained in the distillation of this larger quantity of hydrocarbon, the discrepancy is readily explained. Although the breaking up of spinacene when distilled over sodium does not appear to take place at all rapidly until a temperature corresponding with a pressure of about 40 to 50 mm. is reached, there can be no doubt that a little decomposition does occur even at lower temperatures, and that the hydrocarbon which I originally used for the molecular weight determinations must have been contaminated with a little of the decomposition products of lower boiling point.

It may be recalled that the average results of five analyses of the hydrocarbon given in my previous paper were as follows:

C = 87·75; H = 12·45.

The above results therefore agree well with the formula $C_{29}H_{48}$, which requires C = 87·88; H = 12·12 per cent. M.W. = 396.

Taking the previously determined number for the specific refraction, namely, 0·3394, the molecular refraction is 134·4. Employ-

ing Conrady's average numbers for the atomic specific refractions (D-line), $C_{29}H_{48}$ with six ethenoid linkings requires 134·3. Taking the specific dispersive power of spinacene as 0·0114, its molecular dispersion, $(r\gamma - r\alpha)M$, is 4·51. Taking Eisenlohr's numbers for the atomic dispersion for the α- and the γ-hydrogen lines, the calculated number is 4·21.

As the results of the analysis of the hexahydrochloride which I had previously prepared were in fair agreement with the higher formula, $C_{30}H_{50}$, I determined to prepare a larger quantity of this compound and to submit it to a very thorough process of purification. It was prepared as before, by passing dry hydrogen chloride into a well-cooled solution of spinacene in dry ether. The resulting hexahydrochloride was then purified by dissolving it in warm benzene and adding alcohol until the compound commenced to separate, and finally by crystallising from warm benzene alone. Chlorine estimations were made in each crop of crystals, and the process of recrystallisation was repeated until the chlorine percentage, which showed a tendency to increase, became constant. After the third recrystallisation, the substance was analysed, with the following results:

0·2020 gave 0·2814 AgCl. Cl = 34·45.
0·2145 „ 0·2990 AgCl. Cl = 34·49.
$C_{29}H_{48}$,6HCl requires Cl = 34·60 per cent.

In the process of recrystallisation, the melting point also rose, the final preparation becoming pasty at about 120° and melting to a clear liquid at 126°. During this process of recrystallisation, a small quantity of an oily substance containing about 24 per cent. of chlorine was separated from the mother liquors. It will be seen that the above result is in far better agreement with the formula $C_{29}H_{48}$ than with the formula previously suggested, namely, $C_{30}H_{50}$, which requires Cl = 33·86 per cent. A 5 per cent. solution of the hydrochloride in benzene was found to be optically inactive.

When heated for some time with boiling water, in which it appears to be quite insoluble, no decomposition occurred. When heated, however, for some time with a mixture of alcohol and water, the crystals soon became pasty, and the liquid, after filtering, gave a strong reaction for chloride.

In the course of these experiments, a further quantity of the oily hydrochloride soluble in ether was obtained, but there is some doubt as to the definite character of this compound, and a further study renders it very doubtful whether it constitutes a product intermediate between the hydrocarbon and the crystalline hexahydrochloride.

Decomposition of Spinacene Hexahydrochloride by Heat.

I have previously directed attention to the fact that, when this compound is heated to a temperature above its melting point, hydrogen chloride is liberated. 2·14 Grams of the hydrochloride were introduced into a weighed test-tube, which was connected with a vacuum pump. The tube was then immersed in an oil-bath and heated for four hours to 150°. Hydrogen chloride was freely evolved, particularly at the commencement of the experiment, and at the end of the above time it was found that 0·32 gram of hydrogen chloride had been lost. The heating was then continued, but as the evolution of gas became very slow, the temperature of the bath was raised to 190°, at which temperature it was maintained for seven hours. At the end of this time, a further 0·36 gram of hydrogen chloride had been given off, making a total loss of 0·68 gram, the total amount present in the hydrochloride taken being 0·76 gram. At this point, the evolution of hydrogen chloride had become so slow that the experiment was stopped.

The oil remaining in the tube was fairly mobile and of a pale red colour. The iodine value of this oil was 255·5, and it contained Cl=5·2 per cent. A 10 per cent. solution in benzene was found to be optically inactive.

From this experiment, it would appear that the hydrocarbon left after expelling the hydrogen chloride by heat differs from the original spinacene in being less unsaturated, due probably to the occurrence of some intramolecular change, such as that involved in the conversion of pinene into camphene. The molecular weight of this oil determined by the depression of the freezing point in benzene solution was 479, showing that, in addition to the above intramolecular change, there had been some polymerisation.

Action of Hydrogen Bromide. Spinacene Hexahydrobromide.

Dry hydrogen bromide was passed into a well-cooled solution of spinacene in several times its volume of dry ether. Shortly after the liquid had become saturated, a white substance formed, which appeared to consist of a crystalline substance and an oil. A further quantity of dry ether was added, and the precipitate was separated, washed with ether, and dried. This substance was purified by dissolving it in benzene, adding alcohol until the separation of the compound just commenced, and finally by recrystallisation from benzene alone. After three recrystallisations, the product appeared to be pure, and gave on analysis the following results:

0·2061 gave 0·2640 AgBr. Br = 54·51.

$C_{29}H_{48}$,6HBr requires Br = 54·42 per cent.

As in the case of the hydrochloride, it will be seen that this percentage accords much better with the formula $C_{29}H_{48}$ than with $C_{30}H_{50}$, the theoretical percentage of bromine in the latter case being 53·57.

The hexahydrobromide is a brilliant, white, crystalline compound closely resembling the hydrochloride in appearance as well as in respect of its solubility in the commoner solvents. As in the case of the hexahydrochloride, the yield is not very large, oily compounds being formed at the same time. Thus, in one experiment in which a solution of 5 grams of spinacene in 10 c.c. of ether was saturated with hydrogen bromide and allowed to remain for twenty-four hours, the yield of the hydrobromide did not exceed 6·5 grams. When heated, the crystals soften at about 126° and melt to a clear liquid at about 132°. When heated to a still higher temperature, decomposition occurs, hydrogen bromide being freely evolved.

I have devoted a good deal of care to the purification of the hydrochloride and hydrobromide of spinacene, since these compounds are definite and well crystalline, and consequently afford the best indication as to the correct molecular formula of the hydrocarbon. It will be seen that all the results given above agree well with the formula $C_{29}H_{48}$, and although the other derivatives described in my previous communication are less well defined than the hydrogen haloids and not very easily purified, attention may be directed to the fact that, with one exception, the analytical results in all cases agree better with the formula $C_{29}H_{48}$ than with $C_{30}H_{50}$. This will be more clearly seen by reference to the following numbers:

	Found.	$C_{29}H_{48}$.	$C_{30}H_{50}$.
Spinacene trinitrosochloride:			
Cl =	18·48	18·00	17·50
N =	7·36	7·10	6·92
Spinacene trinitrolpiperidide:			
N =	11·52	11·38	11·20
Spinacene trinitrolbenzylamide:			
N =	10·58	10·45	10·27
Spinacene hexanitrosochloride:			
N =	10·62	10·65	10·46
Cl =	27·42	27·00	26·52
Spinacene nitrosate:			
N =	12·80	12·50	12·30

The single exception referred to above is the dodecabromide, which contains Br = 69·7 as compared with 70·79 per cent. required for the lower molecular formula and 70·07 per cent. for the higher. I have already indicated, however, that the action of bromine on

spinacene is very complicated, both addition and substitution derivatives being simultaneously formed. The bromine compound is, moreover, either insoluble or only very sparingly soluble in the great majority of the ordinary organic solvents, and could only be purified by the addition of alcohol to its solution in tetrachloroethane. It is quite possible, therefore, that this compound has not as yet been obtained in a state of purity.

Action of Nitric Acid on Spinacene.

Nitric acid (D 1·42°) mixed with an equal volume of water was added to spinacene and the mixture warmed. A very vigorous reaction occurred with the evolution of oxides of nitrogen. After the reaction had subsided, water was added, and the solid substance which was formed was collected, washed, and dried. It was purified by dissolving it in aqueous sodium hydroxide and by completely saturating the solution with carbon dioxide. The precipitate which formed was separated by filtration, and the clear filtrate, on acidification with dilute sulphuric acid, gave a further precipitate. The latter substance was almost insoluble in ether or petroleum, but moderately soluble in alcohol. It dissolved readily in glacial acetic acid, from which solvent it was obtained by the gradual addition of water as a pale yellow precipitate.

It is clear that in the above experiment at least two products are formed, and doubtless others could be obtained by modifying the conditions of nitration.

Decomposition of Spinacene by Heat in the Presence of Sodium.

At the commencement of this paper, I referred to the fact that a considerable quantity (about 500 c.c.) of spinacene had been distilled over sodium at temperatures corresponding with a pressure of about 45 mm., and that evidence was obtained that under these conditions some decomposition had occurred. The oil which distilled over between 280° and 295°, and measured about 400 c.c., was submitted to fractional distillation (without sodium) under a pressure of about 40 mm. The following four fractions were finally obtained:

(1) 84—88° (about 60 c.c.).
(2) 155—175° (about 60 c.c.).
(3) 220—275° (about 80 c.c.).
(4) 295—298° (about 150 c.c.).

An almost colourless, viscous substance remained in the flask.

The first of the above fractions, which consisted of a fragrant,

mobile liquid, was purified by steam distillation, followed by fractional distillation. The greater portion (about 50 c.c.) boiled constantly at 69°/20 mm.:

0·1097 gave 0·3470 CO_2 and 0·1286 H_2O. C=86·26; H=13·02.
0·1121 ,, 0·3555 CO_2 ,, 0·1301 H_2O. C=86·48; H=12·89.

From the above, it was clear that this liquid consisted of a hydrocarbon and contained about 0·6 per cent. of oxygen. It was therefore redistilled several times over sodium, and the portion boiling at 51—54°/10 mm. again submitted to analysis:

0·1291 gave 0·4120 CO_2 and 0·150 H_2O. C=87·02; H=12·90.
$C_{10}H_{18}$ requires C=87·0; H=13·0 per cent.

This hydrocarbon boils under the ordinary pressure at 170—175°, a little polymerisation apparently occurring during the process. It is optically inactive. The following molecular weight determination was made by the cryoscopic method:

0·4021 in 16·36 benzene gave $\Delta^t = -0·909°$. M.W.=135.
$C_{10}H_{18}$ requires M.W.=138.

Its specific gravity at 15°/15°=0·8149 and at 20°/20°=0·8125. Its index of refraction at 15°=1·4588 and at 20°=1·4565.

Its specific refraction calculated by the $\frac{n^2-1}{(n^2+2)d}$ formula is 0·3353 and the molecular refraction is 46·3.

Taking Conrady's average numbers for the atomic specific refractions (*D*-line), $C_{10}H_{18}$ with one ethenoid linking requires 45·8.

The following estimations were made of the amount of bromine capable of uniting with the hydrocarbon. The bromine was dissolved in carbon tetrachloride and added to a carbon tetrachloride solution of the hydrocarbon under water, the liquid being cooled by means of ice. By working in this way, a correction could be made for the small amount of hydrogen bromide formed as the result of simultaneous substitution. The following are the results of two experiments:

	A.	*B.*
Substance taken	0·1878 gram	0·1348 gram
Bromine uniting with hydrocarbon...	0·2264 ,,	0·1646 ,,

Both these numbers are in close agreement with the addition of two atoms of bromine to one molecule of the hydrocarbon.

All these results point to this substance being a *cyclo*dihydroterpene, and its properties appear to suggest that it may prove to be identical with *cyclo*dihydromyrcene or with *cyclo*linaloolene. It may be of interest to give for purposes of comparison the physical

properties of *cyclo*dihydromyrcene (*Ber.*, 1901, **34**, 3128) and of *cyclo*linaloolene (*Ber.*, 1894, **27**, 2521):

	Hydrocarbon from spinacene.	*cyclo*Dihydro-myrcene.	*cyclo*Lina-loolene.
Molecular formula	$C_{10}H_{18}$	$C_{10}H_{18}$	$C_{10}H_{18}$
Boiling point	170—175°	169—172°	165—167°
Specific gravity	0·815	0·828	0·811
Refractive index	1·459	1·462	1·460
Number of atoms of bromine added	Two	Two	Two

Had time permitted, specimens of *cyclo*dihydromyrcene and of *cyclo*linaloolene would have been prepared for the purpose of making a fuller comparison. This I hope will be done at some future time. In the above work, steps were taken to make it quite clear that this terpenic hydrocarbon was not formed by the action of sodium on the small amount of oxygenated constituent occurring in the spinacene used. To this end, the spinacene, after having been distilled over a considerable excess of sodium under 10 mm. pressure, was then redistilled over a further quantity of sodium under 40 mm. pressure. From the distillate, the terpenic hydrocarbon described above was separated by steam distillation. The recovered and unchanged spinacene was then for a third time distilled over sodium under 40 mm. pressure, with the result that a further quantity of the terpenic hydrocarbon was obtained. There can, therefore be no reasonable doubt that this *cyclo*dihydroterpene does, in fact, result from the breaking up of the spinacene molecule. The view which I ventured to put forward in my first communication, that spinacene would prove to be related in some way to the terpenes, is therefore correct. The presence in large quantities in fish-liver oil of a complex hydrocarbon closely related to the terpenes is, I think, of very considerable interest both from the chemical and from the physiological points of view. In this connexion, it may be recalled that there is very strong evidence that cholesterol, a substance having nearly the same number of carbon atoms in its molecule as spinacene and occurring also in fish-liver oils, is a complex terpene compound.

The second fraction obtained from the decomposition of spinacene was also a fragrant, tolerably mobile liquid, boiling at 109—115°/10 mm., having an average molecular weight of about 190 and a specific gravity at 15°/15° = 0·868 and at 20°/20° = 0·865. This, as well as the viscous products left in the distillation flask, which doubtless consist of polymerisation products formed during the process, will, it is hoped, be subjected later on to a further study. Except perhaps in one direction in which results of industrial

importance may be anticipated, the further examination of spinacene and its derivatives will have to remain in abeyance until more normal conditions again prevail.

I desire to express my thanks to Miss D. J. Minter and Mr. C. W. McHugo for valuable assistance in connexion with this work.

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ALDGATE, E.C.3.
[*Received, May 2nd*, 1918.]

XL.—*Metallic Derivatives of Alkaloids.*

By JITENDRA NATH RAKSHIT.

HAVING prepared the metallic derivatives of acid amides (T, 1913, **103**, 1557) it was thought that the metallic derivatives of alkaloids could be obtained by a similar method. The sodium and potassium derivatives of codeine and narcotine and the sodium derivative of cotarnine were obtained by boiling the alkaloids with the respective metals in benzene, and the calcium derivative of morphine was isolated from the solution of morphine in lime-water or from its alcoholic solution, prepared by titurating morphine with an excess of slaked lime in alcohol. Of the metallic derivatives, those of narcotine require special mention; there is no hydroxyl group present in the molecule, and there is no hydrogen atom attached to the nitrogen that could be displaced by the metals, as is generally represented to be the case with basic or quasi-basic nitrogenous organic compounds.

Sodium Codeine.

A mixture of 200 c.c. of benzene, 5 grams of freshly cut sodium, and 10 grams of powdered anhydrous codeine was boiled under reflux. At the beginning of the experiment, a very faint ammoniacal odour was perceived at the open end of the condenser, and this continued until the end of the operation. Within ten minutes the benzene turned brownish-yellow, and after half an hour it became opaque. After the mixture had boiled for ten hours, the pieces of sodium were covered with a thin layer of a reddish-brown substance, and the boiling was discontinued. On cooling, the contents of the flask set to a viscous mass like brown jelly, which was collected, pressed between filter paper, and kept

over night in a desiccator over sulphuric acid, when it dried tc a brownish-yellow powder:

0·3537 gave 0·0800 Na_2SO_4. Na = 7·32.

$C_{18}H_{20}O_3NNa$ requires Na = 7·18 per cent.

Sodium codeine is readily soluble in water, giving a brownish-yellow, turbid solution which does not become clear by filtration, but the turbidity disappears on the addition of dilute hydrochloric acid, and the colour is also considerably discharged. It is soluble in alcohol, but insoluble in ether, benzene, or chloroform, and is specifically lighter than the last solvent. The compound is slightly deliquescent; on exposure to the air, it absorbs moisture and becomes viscid, but when left in that condition for a long time it does not appear to change. Its aqueous solution does not give any precipitate with Mayer's reagent, but on acidifying the mixture, an immediate curdy, yellow precipitate is obtained.

Potassium Codeine.

Ten grams of dry powdered codeine were dissolved in 200 c.c. of benzene, and the solution was boiled with 10 grams of potassium as before. The potassium melted and formed smaller shining balls, around which a brisk evolution of gas took place. As in the former experiment, a faint ammoniacal odour was always perceived at the open end of the condenser. Within an hour the benzene gradually assumed a reddish-brown colour, and soon afterwards red crystals began to separate. The boiling was continued until a voluminous mass of crystals separated, which were collected, washed three times with boiling benzene, pressed between filter paper, and kept overnight in a desiccator over sulphuric acid. About 5 grams of the substance were powdered, added to 50 c.c. of benzene, and the mixture was gently boiled for five minutes. It was then filtered whilst hot, and the residue washed three times with boiling benzene to remove codeine, being finally pressed between filter paper and dried in a desiccator over sulphuric acid:

0·6000 gave 0·1590 K_2SO_4. K = 11·88.

$C_{18}H_{20}O_3NK$ requires K = 11·59 per cent.

Potassium codeine dissolves in water, giving a clear solution; it is soluble in alcohol, sparingly so in chloroform, and insoluble in ether or benzene.

Sodium Narcotine.

Five grams of narcotine were boiled with 200 c.c. of benzene and 5 grams of clean sodium; a faint ammoniacal odour was per-

ceived, and the colour of the liquid became brown. After boiling for three daily periods of five hours each, some crystals were deposited, which were collected, washed with hot benzene, pressed between filter paper, and kept overnight in a desiccator, when a reddish-yellow powder was obtained:

0·4110 gave 0·7400 Na_2SO_4. Na=5·82.

$C_{22}H_{22}O_7NNa$ requires Na=5·41 per cent.

Sodium narcotine is a non-deliquescent substance, readily soluble in water to a pale yellow, transparent solution, which does not produce any precipitate with Mayer's reagent, except on acidification. It is soluble in alcohol or chloroform, and almost insoluble in ether or benzene. Nothing could be extracted from its aqueous solution by benzene or ether. When the solution was boiled, however, a slight turbidity was observed, which increased on passing carbon dioxide; the precipitate was collected, washed, and dried, when it melted at 175°. Narcotine also separated in colourless, needle-shaped crystals when the solution was kept in an open flask for six or seven days, but the alkaloid was completely and readily recovered as a colourless, crystalline powder by dissolving the compound in ammonium chloride. It was collected, washed, dried, and recrystallised from benzene, when it melted at 175° and had all the properties of pure narcotine.

Potassium Narcotine.

In the preparation of other metallic derivatives, excess of the metals were used as a rule, but with the potassium derivative of narcotine considerable difficulty was experienced in obtaining the new compound free from unchanged metal. After a part of the reaction was completed, the molten potassium disintegrated into very small pieces, which were never completely separated from the derivative, but became entangled with the crystals of the new compound and did not settle down separately when cooled. To avoid this difficulty, excess of the alkaloid was employed, and the unchanged narcotine was removed by washing with benzene. Five grams of potassium and 40 grams of narcotine were boiled with 300 c.c. of benzene under reflux. Within an hour the potassium derivative began to be deposited as a brownish-yellow powder. The boiling was continued for twelve hours, during which period the usual faint ammoniacal odour was noticed; the mixture was filtered hot, and the precipitate washed five times with boiling benzene, care being taken to keep it covered with liquid, since the substance rapidly absorbs moisture, becoming nacreous,

and then cannot be filtered; the compound also undergoes slight decomposition. The washing with hot benzene, however, may be continued until the filtrate ceases to give any residue on evaporation. The substance was pressed between filter paper and dried in a desiccator over sulphuric acid:

0·1401 gave 0·0501 K_2SO_4. K=16·00.

$C_{22}H_{21}O_7NK_2$ requires K=15·90 per cent.

Dipotassium narcotine is a bright yellow, crystalline powder readily soluble in alcohol, giving a turbid solution; it dissolves in chloroform, is sparingly soluble in benzene, and insoluble in ether. On shaking its aqueous solution with benzene, only a very small quantity of the alkaloid was extracted by the solvent, but when the mixture was shaken with an excess of ammonium chloride, the benzene dissolved almost the whole of the alkaloid. The benzene solution was separated, washed, dried by potassium carbonate, and evaporated, when there remained a non-crystalline residue melting at 160°. Consequently, the substance thus recovered is not pure narcotine, as was the case with the sodium derivative.

Sodium Cotarnine.

Cotarnine was prepared by oxidising narcotine with dilute nitric acid, a slight modification of the method described by Anderson (*Annalen*, 1853, **86**, 187) being used. A mixture of 70 c.c. of nitric acid (D 1·4) and 200 c.c. of water was cooled to 15°, 25 grams of crystallised narcotine were added, and the whole was shaken continuously until the alkaloid was completely dissolved, the solution being kept in a cool place overnight. The white crystals of opianic acid which had settled at the bottom were collected, and the cotarnine was precipitated from the filtrate by means of potassium hydroxide. The alkaloid was well washed, dried in a desiccator over sulphuric acid, and recrystallised from benzene, when it weighed 6·1 grams.

Ten grams of cotarnine, 5 grams of sodium, and 200 c.c. of benzene were heated under reflux; after four hours crystals began to separate, and the boiling was continued for six hours, when the mixture was set aside overnight for the complete precipitation of crystals. These were collected, washed three times with hot benzene, pressed between filter paper, and dried in a desiccator:

0·0130 gave 0·0115 Na_2SO_4. Na=28·0.

$C_{12}H_{11}O_4NNa_4$ requires Na=28·30 per cent.

Tetrasodium cotarnine is a hygroscopic, bright yellow, crystalline powder, readily soluble in water, giving a clear solution, soluble

in alcohol or chloroform, sparingly so in ether, and practically insoluble in benzene. This compound showed a behaviour altogether different from that of the allied alkaloids in that its aqueous solution gave a precipitate with Mayer's reagent, the amount of which slightly increased on keeping the solution for a day or on acidifying the freshly prepared solution. When its saturated aqueous solution was treated with an excess of ammonium chloride, an immediate turbidity was observed, and on keeping overnight, a crystalline precipitate had formed. This was collected, washed, pressed between filter paper, and dried in a desiccator over sulphuric acid, when it melted at 132°.

Calcium Morphinate.

Morphine is well known to be soluble in lime-water, forming calcium morphinate, which was easily isolated by the following process. Thirty grams of pure morphine were triturated with 6 grams of pure calcium hydroxide, 100 c.c. of rectified spirit were added, the whole being well mixed for thirty minutes and then filtered. The pale brown filtrate was transferred to a shallow dish and kept in a desiccator over sulphuric acid; after two days, calcium morphinate separated as a shining, scaly, light powder. The product obtained by substituting water for alcohol was not so pure, and was much darker. The alcoholic product was completely dissolved by alcohol or water, whereas the other left a slight residue, and a clear solution was only obtained from it by filtration. Consequently, the alcoholic product was assumed to be pure:

0·2060 gave 0·0200 CaO. Ca = 6·93.

$(C_{17}H_{18}O_3N)_2Ca$ requires Ca = 6·58 per cent.

A quantity of the substance was dissolved in *N*/10-sulphuric acid, and the excess titrated with *N*/10-sodium carbonate, using methyl-orange as indicator.

0·5 required 32·6 c.c. of *N*/10-acid, whereas this weight of a compound of the above formula requires 33·11 c.c. of *N*/10-acid to neutralise both calcium and morphine.

Calcium morphinate is a brown, non-deliquescent powder readily soluble in water or alcohol, sparingly so in chloroform, and insoluble in ether or benzene. Its aqueous solution gives the usual precipitate of morphine with ammonium chloride, and with Mayer's solution it gives a precipitate only after acidification. It is readily decomposed by carbonic acid, calcium carbonate and morphine being precipitated.

The investigation is being extended to the metallic derivatives of other alkaloids and to the study of the constitution of the compounds described above.

The author desires to express his best thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of the investigation.

OPIUM FACTORY,
GHAZIPORE, INDIA. [*Received, April 10th* 1917.]

XLI.—*Studies in Catalysis. Part IX. The Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems.*

By WILLIAM CUDMORE McCULLAGH LEWIS.

IN previous papers of this series (compare T., 1916, **109**, 796; 1917, **111**, 457), expressions have been obtained, with the aid of the radiation hypothesis, for velocity constants and equilibrium constants as functions of temperature. In the expressions thus obtained, there occur certain proportionality factors which have to be determined by direct comparison with experiment. In the present paper an attempt is made to deal with the problem in a more complete manner by calculating velocity and equilibrium constants in terms of quantities, all of which have a definite physical meaning and may be determined, theoretically, without reference to the actual rate of the chemical reaction itself.

On the basis of statistical considerations, J. Rice (*Rep. Brit. Assoc.*, 1915, 397) has deduced an expression for the reaction velocity and velocity constant in the case of a unimolecular reaction, that is, the spontaneous decomposition of a single molecule. The assumption made by Rice is that the rate of such a reaction is determined by the rate at which the molecules become active in the physical sense. Active molecules, in unimolecular processes, have therefore no real existence. When, however, we deal with multimolecular reactions, it is conceivable that active molecules exist, the rate of the observed reaction depending on the number of collisions per second which take place between active molecules of the participating substances. The concept of active molecules

was first postulated by Arrhenius, but it is only within recent years that the differentiation between active and passive molecules has attained any degree of precision through the introduction of the concept of critical energy and critical increment. The most direct evidence of an experimental kind which we possess at the present time for the existence of active molecules is that afforded by the measurements of Baly and F. O. Rice (T., 1912, **101**, 1475) in the case of the sulphonation of certain aromatic compounds. In this case, the ultimate chemical reaction is multimolecular, probably bimolecular. We may adopt therefore with some confidence the view that active molecules have a real existence in the case of multimolecular reactions. These active molecules differ from the remainder in respect of their internal energy, which is considerably greater than that possessed by an average molecule of the substance at the temperature in question. The fact that the critical energy is high means that only a very small fraction of the total molecules will be active at any moment.

In the case of a bimolecular reaction, such as the decomposition of hydrogen iodide in the gaseous state, the fractional number of hydrogen iodide molecules which exist in the active state may be calculated by the aid of the expression

$$N_a/N = e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N_a denotes the number of active molecules, N the number of passive molecules or the total number of molecules (since N_a is very small compared with N); E is the critical increment reckoned per gram-molecule, that is, the amount of energy which one gram-molecule of the substance must absorb in order to make it reactive, and R and T have their usual significance. This expression is the familiar one obtained on the basis of statistical mechanics for the distribution of molecules in a field of force. The justification for its application to the present case is furnished by the following calculation of the velocity constant of decomposition of gaseous hydrogen iodide.

In Bodenstein's experiments (*Zeitsch. physikal. Chem.*, 1899, **29**, 295), one gram-molecule was present in 22·4 litres. At 556° abs. the observed velocity constant was $9{\cdot}42 \times 10^{-7}$, the unit of time being the minute. On expressing the time in seconds and the concentration in gram-molecules per litre, the velocity constant becomes $3{\cdot}517 \times 10^{-7}$. This number represents the fraction decomposed per second at unit concentration.

We have now to calculate the velocity constant on the basis of the concept of active molecules, the equilibrium concentration of which is assumed to be given at all stages of the observed reaction

by equation (1). From the temperature-coefficient* of the reaction, it is calculated that the critical increment per gram-molecule is 22,000 cals. Hence, employing equation (1), it is found that the fraction of one gram-molecule which exists in the active state at 556° abs. is $2{\cdot}218 \times 10^{-9}$. If there is one gram-molecule of hydrogen iodide present in 1 litre, then this number represents the fractional number of active molecules. Since there are $6{\cdot}1 \times 10^{23}$ molecules in one gram-molecule, the actual number of active molecules per litre is $1{\cdot}35 \times 10^{15}$, or $1{\cdot}35 \times 10^{12}$ per c.c.

On the kinetic theory, the number of collisions per c.c. per second between like (active) molecules is given by the expression

$$\sqrt{2}\,.\,\pi\,.\,\sigma^2\,.\,u\,.\,N_a{}^2$$

where N_a is the number of active molecules per c.c., u the mean velocity of translation per molecule, and σ the distance within which two molecules approach one another during a collision. Physical theory has not yet succeeded in defining σ with precision, beyond the fact that it is of the order of magnitude of the radius or diameter of the molecule. Such being the case, we shall take a mean value, 2×10^{-8} cm., and employ this in all cases examined. Naturally, this will introduce a certain error into the results, but its magnitude will not affect the general question of the verification of the method of treatment adopted.

In the case of hydrogen iodide at 556° abs., $u = 3{\cdot}3 \times 10^4$ cm. per second. The value of N_a we have already calculated to be $1{\cdot}35 \times 10^{12}$ per c.c. Hence the number of collisions per c.c. per second between the active molecules is $1{\cdot}065 \times 10^{14}$, or the number of collisions per litre is $1{\cdot}065 \times 10^{17}$. At each collision between active molecules, two such molecules react. Hence the number of molecules of hydrogen iodide which react per second per litre is $2{\cdot}13 \times 10^{17}$. Expressing this as a fraction of one gram-molecule, we obtain $2{\cdot}13 \times 10^{17}/6{\cdot}1 \times 10^{23} = 3{\cdot}5 \times 10^{-7}$. This should be the velocity constant of the reaction expressed in gram-molecules per litre per second. The observed value is $3{\cdot}517 \times 10^{-7}$. The agreement is very satisfactory, especially in view of the possible error in σ. This calculation serves to substantiate the concept of active molecules defined in the above sense.

The foregoing calculation may be carried out in a somewhat different manner which leads directly to the differential equation expressing the reaction velocity. Thus the number of molecules which react per c.c. per second is given by:

$$2\sqrt{2}\pi\sigma^2 u N_a{}^2.$$

* This is the most direct means of obtaining the critical increment. It may also be obtained from the position of the effective absorption band in the spectrum of the substance provided the data are available.

Hence the number of molecules which react per litre per second is given by:

$$2000\sqrt{2}\pi\sigma^2 u N_a^2.$$

N_a is the number of active molecules per c.c. Hence the number of active molecules per litre is 1000 N_a. If N_0 be the number of molecules in one gram-molecule, the number of active gram-molecules per litre is 1000 N_a/N_0. If we denote this by C_a, then $N_a=N_0C_a/1000$, or $N_a^2=N_0^2C_a^2/10^6$. Hence the number of molecules which react per litre per second is:

$$2000\sqrt{2}\pi\sigma^2 u N_0^2 C_a^2/10^{-6}.$$

The number of gram-molecules which react per litre per second is $1/N_0$ of the above quantity. That is, the number of gram-molecules which react per litre per second is

$$2000\sqrt{2}\pi\sigma^2 u N_0 C_a^2/10^6.$$

From equation (1), it follows that $C_a=Ce^{-E/RT}$, where C is the total concentration or number of gram-molecules of hydrogen iodide per litre. Hence the rate of the observed reaction is given by:

$$-dC/dt=5{\cdot}40\times10^{21}\,.\,\sigma^2\,.\,u\,.\,C^2\,.\,e^{-2E/RT}.$$

But the rate, $-dC/dt=k_{\text{obs.}}\,.\,C^2$,
where $k_{\text{obs.}}$ is the velocity constant experimentally determined. Hence, $k_{\text{obs.}}$ (in gram-molecules per litre, per second)

$$=5{\cdot}40\times10^{21}\,.\,\sigma^2\,.\,u\,.\,e^{-2E/RT} \quad . \quad . \quad . \quad . \quad (2)$$

By making use of the concept of active molecules, we can calculate the velocity constants of decomposition of hydrogen iodide over the temperature range corresponding with Bodenstein's observations. The following table contains the calculated and observed velocity constants expressed in gram-molecules per litre per second.

Decomposition of Hydrogen Iodide.

T.	$u\times10^{-4}$	Fraction of one gram-molecule in the active state $=e^{-E/RT}$.	$e^{-2E/RT}$.	k calculated [equation (2)].	k observed.
556°	3·30	$2{\cdot}218\times10^{-9}$	$4{\cdot}898\times10^{-18}$	$3{\cdot}5\ \times10^{-7}$	$3{\cdot}517\times10^{-7}$
575	3·356	$2{\cdot}704\times10^{-9}$	$1{\cdot}820\times10^{-17}$	$1{\cdot}319\times10^{-6}$	$1{\cdot}217\times10^{-6}$
629	3·510	$2{\cdot}244\times10^{-8}$	$5{\cdot}012\times10^{-16}$	$3{\cdot}800\times10^{-5}$	$3{\cdot}02\ \times10^{-5}$
647	3·559	$3{\cdot}656\times10^{-8}$	$1{\cdot}318\times10^{-15}$	$10{\cdot}23\ \times10^{-5}$	$8{\cdot}587\times10^{-5}$
666	3·612	$5{\cdot}970\times10^{-8}$	$3{\cdot}548\times10^{-15}$	$2{\cdot}768\times10^{-4}$	$2{\cdot}195\times10^{-4}$
683	3·657	$8{\cdot}995\times10^{-8}$	$8{\cdot}128\times10^{-15}$	$6{\cdot}421\times10^{-4}$	$5{\cdot}115\times10^{-4}$
700	3·702	$1{\cdot}337\times10^{-7}$	$1{\cdot}778\times10^{-14}$	$1{\cdot}422\times10^{-3}$	$1{\cdot}157\times10^{-3}$
716	3·744	$1{\cdot}905\times10^{-7}$	$3{\cdot}548\times10^{-14}$	$2{\cdot}87\ \times10^{-3}$	$2{\cdot}501\times10^{-3}$
781	3·912	$6{\cdot}918\times10^{-7}$	$4{\cdot}786\times10^{-13}$	$4{\cdot}04\ \times10^{-2}$	$3{\cdot}954\times10^{-2}$
1000	4·42	$1{\cdot}545\times10^{-5}$	$2{\cdot}371\times10^{-10}$	22·63	—

The agreement between the observed and calculated values is satisfactory. The number of active molecules per c.c. rises from $1 \cdot 35 \times 10^{12}$ at 556° abs. to $4 \cdot 22 \times 10^{14}$ at 781° abs. Further, it is seen that at 556° abs., when the total concentration is one gram-molecule per litre, the ratio

$$\frac{\text{number of effective collisions per c.c. per second}}{\text{total number of collisions per c.c. per second}} = \frac{1 \cdot 065 \times 10^{14}}{2 \cdot 18 \times 10^{31}}$$
$$= 4 \cdot 9 \times 10^{-18}.$$

By the term effective collision is meant, of course, the number of collisions between active molecules. This ratio is seen to be an exceedingly small quantity. This quantity may be called conveniently the 'chemical efficiency' of the reaction, since it denotes the number of chemically effective collisions expressed as a fraction of the total number of collisions in the same time. This quantity, as we would expect, increases rapidly with the temperature. Thus, at 781° abs., the chemical efficiency of the reaction considered is $4 \cdot 8 \times 10^{-13}$. At a very high temperature, the upper limit of the efficiency, namely, unity, should be attained theoretically. This temperature must be such that the quantity $e^{-E/RT}$ shall be unity. At 2000° abs., the value of $e^{-E/RT}$ would be $3 \cdot 9 \times 10^{-3}$, and therefore the number of active molecules per c.c., when one gram-molecule is present in one litre, is $2 \cdot 38 \times 10^{18}$. The chemical efficiency is therefore $1 \cdot 5 \times 10^{-5}$. We conclude, therefore, that over any temperature range amenable to experiment in the above reaction the chemical efficiency will be a small quantity.

Bodenstein (*loc. cit.*) has also measured the velocity of union of hydrogen and iodine, and has shown it to be a bimolecular reaction. From the temperature-coefficient, it is easily calculated that the sum of the critical increments per gram-molecule of hydrogen and of iodine is 40,000 cals. This quantity is the analogue of the term $2E$ in the case of the bimolecular decomposition of hydrogen iodide. The quantity 40,000 cals. is made up of two terms, namely, the respective increments of hydrogen and iodine, but at the present stage we do not know each of these terms separately. This is unnecessary, however, for the immediate object in view. It may be noted that the critical increment here referred to is not the critical increment of complete dissociation of hydrogen and of iodine into the atomic state. It will be shown later that the total energy necessary to effect complete dissociation of one gram-molecule of hydrogen and the same mass of iodine is (87,000 + 41,000), or 128,000 cals. The quantity, 40,000 cals., corresponds with a partial activation or polarisation of the hydrogen and iodine molecules sufficient to allow them to react on collision. The partly

activated molecules have a real existence, the system being quite analogous to the partly activated molecules of hydrogen iodide.

On the kinetic theory, the number of collisions per second per c.c. between two unlike molecules is given by the expression:

$$\pi \,.\, \sigma^2 \,.\, N_1 \,.\, N_2 \,.\, \sqrt{u_1^2 + u_2^2},$$

where σ is the average distance to which the molecules approach during a collision, u_1 and u_2 are the mean velocities of translation of the two kinds of molecules, and N_1 and N_2 are the number of active molecules of each kind present in unit volume. The value 2×10^{-8} is assigned to σ. Following the same line of argument as that employed in the deduction of equation (2), we find that the bimolecular velocity, expressed in gram-molecules per litre per second, is given by:

$$-dC/dt = 3{\cdot}8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} \times C_{H_2} \,.\, C_{I_2} \,.\, e^{-40{,}000/RT}$$

or,

$$k_{\text{obs.}} = 3{\cdot}8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} \,.\, e^{-40{,}000/RT} \quad . \quad . \quad (2a)$$

The following table contains the values of the velocity constants calculated by means of equation (2*a*) and those observed by Bodenstein.

Union of Hydrogen and Iodine.

T abs.	$\sqrt{u_1^2 + u_2^2} \times 10^{-4}$	$e^{-40{,}000/RT}$.	k calculated by equation (2*a*).	k observed.
556°	26·5	$1{\cdot}862 \times 10^{-16}$	$7{\cdot}39 \times 10^{-5}$	$4{\cdot}44 \times 10^{-5}$
629	28·2	$1{\cdot}23 \times 10^{-14}$	$5{\cdot}19 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$
666	29·0	$7{\cdot}24 \times 10^{-14}$	$3{\cdot}14 \times 10^{-2}$	$1{\cdot}415 \times 10^{-2}$
700	29·7	$3{\cdot}16 \times 10^{-13}$	$14{\cdot}0 \times 10^{-2}$	$6{\cdot}42 \times 10^{-2}$
781	31·4	$6{\cdot}31 \times 10^{-12}$	2·97	1·336

The agreement between observed and calculated values is moderate. The concordance is evidently limited mainly by the degree of approximation in the value taken for σ. In general, the theoretical basis upon which the calculations are founded may be regarded as justified.*

Stegmüller (*Zeitsch. Elektrochem.*, 1910, **16**, 85) has measured, by an electromotive force method, the equilibrium constant of the hydrogen iodide reaction at much lower temperatures than those with which Bodenstein's measurements correspond. By employing equations (2) and (2*a*), it should be possible to calculate the equilibrium constant at any temperature provided the gases do not deviate seriously from the perfect gas. The following table con-

* From the above data it is found that by setting $\sigma = 1{\cdot}34 \times 10^{-8}$ cm. the calculated and observed values of the velocity constants become nearly identical. This value has been employed in the table dealing with Stegmüller's results.

tains the values so calculated and those obtained by Stegmüller. Stegmüller's values have been recalculated to give the equilibrium constant in the form $C_{H_2} \times C_{I_2}/C^2_{HI}$. The velocity constants are expressed in gram-molecules per litre per second.

Equilibrium Constant of the Hydrogen Iodide Reaction at Low Temperatures.

T abs.	Bimolecular velocity constant of decomposition (equation 2).	Bimolecular velocity constant of union (equation 2*a*) ($\sigma = 1 \cdot 34 \times 10^{-8}$)	Equilibrium constant calculated.	Equilibrium constant, Stegmüller.
304·6°	$1 \cdot 356 \times 10^{-21}$	$2 \cdot 51 \times 10^{-18}$	$5 \cdot 4 \times 10^{-4}$	$11 \cdot 9 \times 10^{-4}$
328·2	$2 \cdot 62 \times 10^{-19}$	$3 \cdot 0 \times 10^{-16}$	$8 \cdot 7 \times 10^{-4}$	$20 \cdot 3 \times 10^{-4}$
354·6	$4 \cdot 123 \times 10^{-17}$	$2 \cdot 98 \times 10^{-14}$	14×10^{-4}	$38 \cdot 3 \times 10^{-4}$

The calculated equilibrium constants are between one-half and one-third of the observed values. Closer agreement is obtained in other reactions, considered later. As illustrated in the above table, we are able to calculate with a moderate degree of accuracy the velocity constants of the opposing reactions, quantities which, owing to their exceedingly small magnitude over the range of temperature considered, could not be determined experimentally.

So far, we have dealt with reaction velocity in gaseous systems from the point of view of molecular statistics. We have now to consider it from the point of view of the radiation hypothesis.

We have seen already that the critical increment of the bimolecular decomposition of hydrogen iodide is 22,000 cals. per gram-molecule. On the radiation hypothesis, this energy is supplied by $N_0 h\nu$ quanta, where N_0 is the number of molecules in one gram-molecule, h is Planck's constant, and ν the frequency of the effective radiation. It is easily calculated that the required frequency is $2 \cdot 33 \times 10^{14}$, or $\lambda = 1 \cdot 3\,\mu$, in round numbers. If the above reasoning is correct, gaseous hydrogen iodide should exhibit an absorption band at this wave-length, especially if the gas be heated. The author is unaware of any experimental data bearing on this point.

On the basis of the quantum theory, Planck has considered the problem of the relation of emission to non-emission by an oscillator (compare Planck, "Theory of Heat Radiation," English trans., p. 164). According to Planck, the ratio of the probability that no emission takes place to the probability that emission does take place is proportional to the radiation density u_ν of the frequency ν. The ratio is given by the expression $p \, . \, u_\nu$. The factor p is shown to be identical with the expression $c^3/8\pi h n^3 \nu^3$, where c is

the velocity of light in a vacuum and n the refractive index of the system for the frequency ν. For gaseous systems, n is practically unity. It will be observed that the probability that no emission takes place is inversely as the cube of the frequency. So long as no emission takes place, the energy of the oscillator, and therefore of the whole atom or molecule containing one or more oscillators, remains high. Such a molecule will correspond with an active one in the chemical sense. It is reasonable, therefore, to apply Planck's principle to a case such as the decomposition of hydrogen iodide and write,

$$\frac{\text{the number of chemically active molecules in existence}}{\text{the number of passive molecules}}=p\,.\,u_\nu$$

Since the number of active molecules is exceedingly small, the number of passive molecules is practically identical with the total number present, or, employing the symbols used previously,

$$Na/N=p\,.\,u_\nu.$$

This relation expresses the fact that the higher the radiation density the greater is the number of molecules in the active state. We may also write this expression in the form:

Fraction of one gram-molecule in the active state $=pu_\nu$.

Further, for the short infra-red, visible and ultra-violet regions,

$$u_\nu=\frac{8\pi hn^3\nu^3}{c^6}e^{-N_0h\nu/RT},$$

Hence,

$$p\,.\,u_\nu=e^{-N_0h\nu/RT}$$

or the fraction of one gram-molecule in the active state is $e^{-Nh_0\nu/RT}$ But $N_0h\nu=E$, the critical increment per gram-molecule. Hence the fraction of one gram-molecule in the active state $=e^{-E/RT}$, which is the expression already obtained on the statistical mechanical basis, and verified by the experimental data. We are justified, therefore, in making the assumption that the chemically active fraction of each gram-molecule of hydrogen iodide is given by the expression $p\,.\,u_\nu$. This should hold good for any substance which reacts in the bimolecular, or in general the multimolecular manner. It is only in such cases that active molecules have any real existence. In the case of unimolecular reactions, active molecules do not exist as such.

In a bimolecular reaction of the type considered, if C denotes the total number of gram-molecules in a given volume, say 1 litre, then the number of active gram-molecules in the same volume may be expressed by

$$C\,.\,p\,.\,u_\nu \text{ or } C\,.\,e^{-N_0h\nu/RT} \text{ or } C\,.\,e^{-E/RT}$$

On the purely kinetic basis, we have seen that the rate of reaction between like molecules in a bimolecular reaction per litre per second is:

$$-dC/dt = 5{\cdot}4 \times 10^{21} \,.\, \sigma^2 \,.\, u \,.\, C^2 e^{-2E/RT}.$$

The term $C^2 \,.\, e^{-2E/RT}$ is evidently identical with $C^2 \,.\, p^2 \,.\, u_\nu^{\,2}$, so that the rate of reaction may be written,

$$-dC/dt = 5{\cdot}4 \times 10^{21} \,.\, \sigma^2 \,.\, u \,.\, p^2 \,.\, C^2 \,.\, u_\nu^{\,2}.$$

That is, the rate of the observed bimolecular reaction depends on the square of the radiation density, a conclusion which is in agreement with the assumption made in earlier papers in connexion with bimolecular reactions. The advantage of the present mode of treatment is, however, that all the factors which go to make up the observed velocity constant are calculable quantities. It is evident that the observed velocity constant, expressed in gram-molecules per litre per second, for a bimolecular reaction involving like molecules is given by:

$$k_{\text{obs.}} = 5{\cdot}4 \times 10^{21} \,.\, \sigma^2 \,.\, u \,.\, p^2 \,.\, u_\nu^{\,2},$$

or

$$k_{\text{obs.}} = 5{\cdot}4 \times 10^{21} \,.\, \sigma^2 \,.\, u \,.\, e^{-2N_0 h\nu/RT}.$$

It is obvious that differentiation of this expression with respect to temperature yields the well-known Arrhenius equation as a first approximation.

In a bimolecular reaction such as that considered, the function of the radiation of the absorbable type is to maintain a certain number of molecules in the chemically active state, a state which means high energy content. The number of active molecules at any moment is the difference between their rate of production and their rate of disappearance. Their rate of disappearance is due to retransformation of some into the passive state, and at the same time the transformation of others in the ordinary chemical sense into the resultants. It is simply the number of active gram-molecules *in existence* at any moment which has been written as $C \,.\, p \,.\, u_\nu$. The actual rate of production of active molecules per second is a quantity necessarily much greater than this. An attempt will now be made to estimate this rate.

In the case of hydrogen iodide at a concentration of one gram-molecule per litre at 556° abs., we have seen that the number of active molecules maintained by the radiation in the active state per litre is $1{\cdot}35 \times 10^{15}$. The number of active molecules which react per second per litre is $2{\cdot}13 \times 10^{17}$. If we denote by R_1 the rate of production of active molecules per second per litre, by R_2 the rate of chemical reaction ($2{\cdot}13 \times 10^{17}$), and by R_3 the rate at

which active molecules are retransformed into passive molecules per litre per second, we have the relation:

$$R_1-(R_2+R_3)=1{\cdot}35\times10^{15}.$$

In order to maintain the active molecules and allow for the rate of the observed reaction, the minimum rate of production of active from passive molecules is $>2{\cdot}13\times10^{17}$. The true rate may, however, be much greater than this lower limit. It is evident that the rate of production of active molecules must depend on the radiation density u_ν, but it is evident the rate is not given by the expression $N_0 . p . u_\nu$, for this would only account for a production of $1{\cdot}35\times10^{15}$ active molecules per second from one gram-molecule. A quantity having a higher numerical value than $N_0 . p . u_\nu$ is required. The terms N_0 and u_ν would be expected to remain unaltered, and we are limited to some function of p. It will be shown later, in connexion with the dissociation of iodine, bromine, and chlorine, that the experimental values can be accounted for if we assume provisionally that the required function is 10^3p^2.* With this assumption, the rate of production of active molecules from one gram-molecule is $N_0 . 10^3 . p^2 . u_\nu$. Since u_ν itself can be written as $\frac{1}{p}e^{-N_0h\nu/RT}$, our assumption means that the rate of production of active molecules is given by $10^3 . N_0 . pe^{-N_0h\nu/RT}$, or $10^3 . N_o . p . e^{-E/RT}$. This expression should be the correct one for any spontaneous unimolecular reaction, for in such a case the process of activation is identical with the chemical reaction. That is, the velocity constant of a unimolecular reaction should be given by:

$$k_{\text{obs.}}=10^3 . p . e^{-E/RT}$$

We shall now apply this expression to the calculation of the rate of production of active molecules of hydrogen iodide. The term p is given by $c^3/8\pi hn^3\nu^3$, and since, for the process considered, $E=N_0h\nu=22{,}000$ cals. per gram-molecule, the frequency ν must be $2{\cdot}33\times10^{14}$. Further, the system is gaseous, and therefore the refractive index is practically unity. Hence $p=1{\cdot}307\times10^{13}$. Hence the number of active molecules produced per second from one gram-molecule of hydrogen iodide at 556° abs. $=6{\cdot}1\times10^{23}\times1{\cdot}307\times10^{13}\times2{\cdot}218\times10^{-9}=1{\cdot}768\times10^{28}$. If we divide this number by $6{\cdot}1\times10^{23}$, we obtain the fraction of one gram-molecule activated per second. A rate of this magnitude is quite possible in the sense that it is sufficient to account for the observed rate of the

* This function will be dealt with in a later paper, in which an alternative expression, having a similar numerical value, but possessing a more precise physical significance, will be given.

bimolecular reaction, and likewise for the maintenance of the free active molecules. Since the rate of production of active molecules is considerably greater than the sum of the two effects just mentioned, it follows that the rate at which active molecules are retransformed into passive is likewise of the order 10^{28}. If these extremely high opposing velocities exist, we are led to the conclusion that the equilibrium between active and passive molecules is attained practically instantaneously. This is in agreement with experience, but, of course, such evidence is very inconclusive. Quantitative evidence is furnished by the calculation of the equilibrium constant in the case of the dissociation of iodine, bromine, and chlorine. This will be considered later.

Whilst the ordinary thermal decomposition of hydrogen iodide is a bimolecular process, Bodenstein has shown (*Zeitsch. physikal. Chem.*, 1907, **61**, 447) that the photochemical decomposition is unimolecular. In this case, the process is the decomposition of hydrogen iodide molecules into atoms of hydrogen and iodine. This is effected by short waves. That is, the process of completely decomposing the hydrogen iodide molecule is a much more difficult one to carry out and requires a greater size of quantum than is required simply to displace the atoms somewhat with respect to one another inside the hydrogen iodide molecule, thereby permitting the bimolecular process to take place. In Bodenstein's experiments on the photochemical decomposition, the hydrogen iodide was exposed to bright sunlight in glass vessels. Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 889) find that hydrogen iodide is decomposed by blue or violet light. More precise knowledge is wanting, but it is evident that the active wave-length is of the order $450\,\mu\mu$, or $\nu = 6{\cdot}66 \times 10^{14}$. That is, the critical increment E' per gram-molecule of hydrogen iodide for the unimolecular decomposition is 63,000 cals. in round numbers. It will be shown later that a more exact value for this quantity is 66,000 cals. This is just three times the increment for the bimolecular reaction. The bimolecular reaction takes place, therefore, more readily, since a molecule will oftener possess the energy corresponding with E than the energy corresponding with E'. This unimolecular process must take place, however, as a thermal effect along with the bimolecular process, for, at any temperature, the radiation density, even at $\nu = 7{\cdot}0 \times 10^{14}$, cannot be entirely wanting. Since, however, the radiation density diminishes rapidly as the frequency increases from the short infra-red into the ultra-violet, the unimolecular reaction, compared with the bimolecular, will remain negligible until very high temperatures are reached. On the basis of the considerations already developed, it is quite possible to calculate what this uni-

molecular decomposition velocity amounts to at any temperature. Thus, the rate of unimolecular decomposition of hydrogen iodide per gram-molecule is given by $10^3 . N_0 . p . e^{-66,000/RT}$, where $p = 4{\cdot}66 \times 10^{11}$. At 556° abs., this rate should be $3{\cdot}12 \times 10^{12}$ molecules per second when one gram-molecule is present initially. Hence the unimolecular velocity constant $= 10^3 . p . e^{-66,000/RT}$ is $5{\cdot}1 \times 10^{-12}$. It will be observed that this is a small quantity compared with the bimolecular velocity constant ($3{\cdot}5 \times 10^{-7}$) under the same conditions. At 781° abs., the unimolecular velocity constant is $1{\cdot}54 \times 10^{-4}$, whilst the bimolecular constant is $4{\cdot}0 \times 10^{-2}$. The conclusion that the unimolecular decomposition is small compared with the bimolecular over the range examined by Bodenstein (556—781° abs.) is in agreement with the fact that the bimolecular formula holds good. We can easily calculate the bimolecular constant at 1000° abs. by the methods already employed at lower temperatures, the value obtained being 22·63. At the same temperature, the unimolecular velocity constant is calculated to be 1·73. At 1200° abs., the unimolecular constant is 435, whilst the bimolecular is 998. It is evident, therefore, that at a temperature somewhat above 1200° abs., the two types of decomposition will occur at the same rate. At this temperature, therefore, the bimolecular formula would be expected to break down.

We now turn to the consideration of unimolecular dissociation, such as that of iodine in the gaseous state into atoms. From the known behaviour of nascent atoms, it may be inferred that their normal state in respect of energy content is sensibly identical with the critical state, so that the exponential term in equation (2) containing the critical increment reduces to unity. Let C_u denote the equilibrium concentration of undissociated molecules of iodine expressed in gram-molecules per litre, and C_i the equilibrium concentration of the iodine atoms in the same units. The rate at which the molecular species dissociates is then given by $C_u . 10^3 . p . e^{-N_0 h\nu/RT}$ or $C_u . 10^3 . p . e^{-E/RT}$. In an earlier paper (T., 1917, **111**, 1086), the value 41,000 cals., per gram-molecule, has been assigned to the critical increment of iodine. The corresponding frequency ν is $4{\cdot}3 \times 10^{14}$, or $\lambda = 700\ \mu\mu$. Hence $p = c^3/8\pi h\nu^3 = 2{\cdot}08 \times 10^{12}$. At $T = 1073$ ($t^\circ = 800^\circ$), the term $e^{-E/RT} = 4{\cdot}385 \times 10^{-9}$. Hence the rate of dissociation, expressed in gram-molecules per litre per second, is $C_u \times 10^3 \times 2{\cdot}08 \times 10^{12} \times 4{\cdot}385 \times 10^{-9} = 9{\cdot}16 \times 10^6 C_u$. The number $9{\cdot}16 \times 10^6$ is the unimolecular velocity constant of dissociation. The rate at which the atoms combine is given by the total collision frequency, for in the case considered, the atoms are all active and every collision is effective. Since there are C_i gram-atoms per litre, the actual number of atoms per c.c. is

$C_i \times 6{\cdot}1 \times 10^{20}$. The collision frequency per c.c. per second is $\sqrt{2} . \pi . u . \sigma^2 . C_i^2 \times 37{\cdot}2 \times 10^{40}$. The average velocity of translation u of one iodine atom at 1073° abs. is $4{\cdot}6 \times 10^4$ cm. per second. Taking σ as 2×10^{-8} cm., the number of collisions per c.c. per second is $3{\cdot}031 \times 10^{31} . C_i^2$. The number of atoms which combine is just twice this quantity, namely, $6{\cdot}062 \times 10^{31} . C_i^2$. Hence the number of *gram*-atoms which combine per second per litre is $9{\cdot}94 \times 10^{10} . C_i^2$. Alternatively, using equation (2) and writing the exponential term as unity, we arrive at the same result. It follows that $C_i^2/C_u = 9{\cdot}16 \times 10^6/9{\cdot}94 \times 10^{10} = 9{\cdot}2 \times 10^{-5}$. Bodenstein and Starck (*Zeitsch. Elektrochem.*, 1910, **16**, 961) have measured the equilibrium constant, C_i^2/C_u, at 1073° abs., with the concentration expressed in gram-molecules per litre, the value obtained being $1{\cdot}29 \times 10^{-4}$. The calculated equilibrium constant agrees well with the observed value. Again, consider the dissociation at 1473° abs. The value of $e^{-E/RT}$ is $8{\cdot}166 \times 10^{-7}$. Hence the rate of dissociation in gram-molecules per second is

$$2{\cdot}08 \times 10^{15} \times 8{\cdot}166 \times 10^{-7}\ C_u.$$

From equation (2), taking σ as 2×10^{-8} and $u = 5{\cdot}38 \times 10^4$, we get for the rate of union of the atoms, expressed in gram-atoms per litre per second, the value $1{\cdot}14 \times 10^{11} \times C_i^2$. Hence

$$C_i^2/C_u = 1{\cdot}699 \times 10^9/1{\cdot}14 \times 10^{11} = 1{\cdot}49 \times 10^{-2}.$$

The observed equilibrium constant is $1{\cdot}02 \times 10^{-2}$.

The foregoing considerations, which are based partly on molecular statistics and partly on the quantum theory of radiation, allow us to calculate with a moderate degree of precision not only the equilibrium constant of a dissociation of a molecule into atoms (a quantity which is amenable in general to experimental determination), but likewise the separate velocity constants which, owing to their great magnitude, cannot be measured directly. The table on p. 484 contains the values of the equilibrium constants and the velocity constants in the above units for the dissociation of iodine over the range of temperature investigated by Bodenstein and Starck.

The agreement between the calculated and observed equilibrium constants is satisfactory. This affords considerable support for the assumptions made as regards the velocity constants. It may be pointed out that the term $e^{-E/RT}$ in this case does *not* represent the number of the active molecules of molecular iodine. No active molecules exist apart from the atoms. The conditions obtaining are quite distinct from those met with in the case of the bimolecular decomposition of hydrogen iodide.

Bodenstein (*Zeitsch. Elektrochem.*, 1916, **22**, 327) has measured

Dissociation of Iodine.

$t°$.	T abs.	$e^{-E/RT}$.	Mean velocity of translation of an iodine atom in cm. per sec. $\times 10^{-4}$.	Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of recombination.	Equilibrium constant (calculated).	Equilibrium constant (observed).
800	1,073°	4.385×10^{-9}	4·6	9.16×10^{6}	9.94×10^{10}	9.2×10^{-5}	1.29×10^{-4}
900	1,173	2.265×10^{-8}	4·83	4.71×10^{7}	1.04×10^{11}	4.5×10^{-4}	4.92×10^{-4}
1,000	1,273	8.995×10^{-8}	5·058	1.87×10^{8}	1.08×10^{11}	1.7×10^{-3}	1.58×10^{-3}
1,100	1,373	2.944×10^{-7}	5·24	6.12×10^{8}	1.13×10^{11}	5.4×10^{-3}	4.37×10^{-3}
1,200	1,473	8.166×10^{-7}	5·38	1.69×10^{9}	1.14×10^{11}	1.49×10^{-2}	1.02×10^{-2}

the dissociation constant of gaseous bromine between 800° and 1200°. He finds that the equilibrium constant, expressed in partial pressure terms, is given by the expression:

$$\log K_p = -10100/T + 1\cdot75 \log T - 0\cdot000409T + 4\cdot726 \times 10^{-8}T^2 + 0\cdot548.$$

Further details are not given in the abstract, which alone is available. At 1000° abs., this expression gives $\log K_p = \bar{5}\cdot336$, whence the equilibrium constant K_c, expressed in gram-molecules per litre, is $2\cdot64 \times 10^{-7}$.

An attempt will now be made to calculate this equilibrium constant. The critical increment E per gram-molecule of bromine is not known with accuracy (compare T., 1917, **111**, 1086). It may be taken to be of the order 50,000 cals. The corresponding frequency $\nu = 5\cdot3 \times 10^{14}$. Hence $p = 1\cdot1 \times 10^{12}$ and

$$e^{-E/RT} = 1\cdot175 \times 10^{-11}.$$

At the equilibrium point, the rate of dissociation of the bromine molecules is $10^3 . p . C_u \; e^{-E/RT} = 10^3 \times 1\cdot1 \times 10^{12} \times 1\cdot175 \times 10^{-11} \times C_u = 1\cdot29 \times 10^4 C_u$, where $1\cdot29 \times 10^4$ is the calculated unimolecular velocity constant of decomposition and C_u is the number of gram-molecules per litre. In dealing with the union of the atoms, we shall again make the assumption that the atoms are all active. At 1000° abs., the average speed u of a bromine atom is $5\cdot6 \times 10^4$ cm. per second. Setting $\sigma = 2\cdot0 \times 10^{-8}$ cm., and employing equation (2), we obtain for the rate of union of the atoms per second per litre the value $1\cdot21 \times 10^{11} C_i^2$, where the numerical coefficient is the bimolecular velocity constant. The equilibrium constant is therefore given by $C_i^2/C_u = 1\cdot29 \times 10^4 / 1\cdot21 \times 10^{11} = 1\cdot0 \times 10^{-7}$. This agrees satisfactorily with the observed value when we consider the possible error in σ and in E.[1]

The dissociation of chlorine has been measured by Pier (*Zeitsch. physikal. Chem.*, 1908, **62**, 417), but the values appear to be much less accurate than those of Bodenstein in the case of bromine and iodine. Thus, the heat of the reaction when calculated from successive values of the equilibrium constant varies in quite an unexpected manner with the temperature. As the possibility of error seems to be less in the higher temperature range, we shall restrict ourselves to this region. Thus, at 1940° abs., the observed degree of dissociation of chlorine is 0·0157, the pressure being 0·5 atmosphere. Hence $K_c = x^2/(1-x)V = 7\cdot8 \times 10^{-7}$. The critical increment of chlorine is taken to be 86,000 cals. per gram-molecule

[1] In the paper referred to, E for bromine was taken to be 57,000 cals. per gram-molecule. Employing the value 50,000 cals., the calculated heat of formation of potassium bromide is in rather better agreement, and the heat of formation of silver bromide in rather worse agreement with the corresponding observed value than are the numbers given in the former paper.

(compare T., 1917, **111**, 1086). Hence at 1940° abs., $e^{-E/RT}=2{\cdot}014\times10^{-10}$. The frequency $\nu=9{\cdot}1\times10^{14}$. Hence $p=2{\cdot}2\times10^{11}$. At the equilibrium point, the rate of dissociation of chlorine is consequently $4{\cdot}43\times10^{4}C_u$, where $4{\cdot}43\times10^{4}$ is the unimolecular velocity constant expressed in gram-molecules per second. The average speed u of a chlorine atom at 1940° abs. is $8{\cdot}3\times10^{4}$ cm. per second. Taking σ as $2{\cdot}0\times10^{-8}$ cm., and using equation (2), we obtain, for the rate of union of the atoms, $1{\cdot}793\times10^{11}C_i^2$, the velocity constant being expressed in gram-molecules per litre per second. Hence the equilibrium constant, C_i^2/C_u should be $4{\cdot}43\times10^{4}/1{\cdot}793\times10^{11}$, or $2{\cdot}47\times10^{-7}$. It will be seen that the calculated and observed values of the equilibrium constant are of the same order of magnitude. The results obtained in the case of the three halogens, iodine, bromine, and chlorine, afford a considerable amount of evidence in favour of the theoretical treatment employed.

In the type of reaction just considered, namely, the dissociation of a molecule into atoms in the gaseous state, the position of equilibrium is given by the relation:

$$10^3\,.\,p\,.\,e^{-E/RT}\,.\,C_u=5{\cdot}40\times10^{21}\,.\,\sigma^2\,.\,u\,.\,C_i^2 \quad . \quad . \quad (3)$$

or

$$K=C_i^2/C_u=\frac{10^3p\,.\,e^{-E/RT}}{5{\cdot}40\times10^{21}\,.\,\sigma^2\,.\,u}$$

where the concentration is expressed in gram-molecules per litre. In a gaseous system p may be written as $1{\cdot}6\times10^{56}/\nu^3$, where ν is the frequency of the radiation responsible for the dissociation process. For a given substance, ν is a constant independent of temperature so long as the mechanism of the process remains the same. We can write the above expression in the form:

$$\log K=-E/RT-\log u+\log 10^3\,.\,p/5.40\times10^{21}\times\sigma^2.$$

The final term on the right-hand side is analogous to the integration constant which occurs in the thermodynamic treatment of mass-action equilibrium. In the present case, however, the final term is calculable quite apart from the reaction itself. On differentiating the above expression with respect to temperature, we obtain:

$$d\log K/dT=E/RT^2-d\log u/dT.$$

The mean velocity of translation of an atom (which has been taken as practically identical with the root-mean-square-velocity) is proportional to the square root of the absolute temperature, u being given by the expression $\sqrt{3RT/M}$, where M is the gram-molecular weight of the atom. Hence

$$d\log K/dT=(E-1/2\,.\,RT)/RT^2.$$

The term $(1/2)RT$ is, in general, small compared with E, and therefore the critical increment in the case of reactions of the above type is practically identical with the heat of dissociation at constant volume. This is the assumption which has been made in the foregoing treatment. If $-Q_v$ denotes the heat absorbed at constant volume per gram-molecule dissociated, we obtain the van't Hoff isochore from the above expression. For the type of reaction considered, the exact relation between the critical increment and the heat of the reaction is given by:

$$-Q_v = E - 1/2 \, . \, RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

We are now in a position to deal with the dissociation of hydrogen. Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 417) finds that the heat of dissociation at constant volume at 3000° abs. is 84,000 cals. per gram-molecule. Hence, from equation (4), we obtain 87,000 cals. as the critical increment per gram-molecule of hydrogen. The corresponding frequency is $9 \cdot 21 \times 10^{14}$, or $\lambda = 325\ \mu\mu$. Hence $p = 2 \cdot 04 \times 10^{11}$. At 2000° abs., $e^{-E/RT} = 3 \cdot 055 \times 10^{-10}$. Hence the rate of dissociation $= 10^3 \, . \, p \, . \, e^{-E/RT} \, . \, C_u = 6 \cdot 23 \times 10^4 C_u$. At 2000° abs., u for one hydrogen atom is $7 \cdot 1 \times 10^5$ cm. per second. Taking $\sigma = 2 \times 10^{-8}$ cm., and using equation (2), the rate of union of hydrogen atoms, assuming all the atoms active, is $1 \cdot 53 \times 10^{12} C_i^2$, the velocity constant being expressed in gram-atoms per litre per second. Hence the equilibrium constant is $4 \cdot 07 \times 10^{-8}$. The degree of dissociation of hydrogen as determined by Langmuir is 0·0033 at 2000° abs. and under one atmosphere's pressure. Hence Langmuir's equilibrium constant, expressed in concentration terms, is $6 \cdot 6 \times 10^{-8}$. This agrees fairly well with the calculated value. The main cause of the discrepancy is probably the fact that in the case of the hydrogen atom, σ is less than 2×10^{-8} cm. If we set $\sigma = 1 \cdot 57 \times 10^{-7}$ cm., the two values of the equilibrium constant become identical. This value of is used in the following table, which contains the values of K obtained by Langmuir and those obtained by the above method of calculation.

Dissociation of Hydrogen.

T abs.	u in cm. per sec. $\times 10^{-5}$	Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of union.	Equilibrium constant, calculated.	Equilibrium constant, Langmuir.
1,500°	6·15	41·66	$8 \cdot 2 \times 10^{11}$	$5 \cdot 1 \times 10^{-11}$	$4 \cdot 6 \times 10^{-11}$
2,000	7·1	$6 \cdot 23 \times 10^4$	$9 \cdot 4 \times 10^{11}$	$[6 \cdot 6 \times 10^{-8}]$	$6 \cdot 6 \times 10^{-8}$
2,500	7·95	$4 \cdot 98 \times 10^6$	$1 \cdot 1 \times 10^{12}$	$4 \cdot 7 \times 10^{-6}$	$5 \cdot 1 \times 10^{-6}$
3,000	8·66	$9 \cdot 26 \times 10^7$	$1 \cdot 2 \times 10^{12}$	$8 \cdot 0 \times 10^{-5}$	$7 \cdot 0 \times 10^{-5}$
3,500	9·37	$7 \cdot 46 \times 10^8$	$1 \cdot 3 \times 10^{12}$	$6 \cdot 0 \times 10^{-4}$	$6 \cdot 1 \times 10^{-4}$
4,000	10·0	$3 \cdot 58 \times 10^9$	$1 \cdot 33 \times 10^{12}$	$2 \cdot 7 \times 10^{-3}$	$2 \cdot 9 \times 10^{-3}$

The agreement throughout is satisfactory. It should be observed, however, that both series of K values are dependent on the numerical value for the heat effect, namely, 84,000 cals. at constant volume. This quantity has been verified approximately by Isnardi (*Zeitsch. Elektrochem.*, 1915, **21**, 405).

The following considerations also afford some support in favour of Langmuir's value for Q_v. We have seen that when hydrogen iodide decomposes in the *uni*molecular manner, the critical increment E' is approximately 63,000 cals. per gram-molecule. Let us suppose that two gram-molecules decompose in this manner, not in the ordinary bimolecular manner. That is, we have the reactions:

$$2HI \longrightarrow 2H + 2I \longrightarrow H_2 + I_2.$$

This will be referred to as the 'atomic' process. Although this is formally the same as the ordinary bimolecular process, the actual mechanism, involving as it does the formation of free atoms, is different, for in the bimolecular process we deal only with a polarisation or partial activation of each of the molecules H_2, I_2, and HI, a process which requires much less energy to reach the respective critical states than is required for the actual dissociation of each molecular species into atoms. Every chemical process, occurring spontaneously, follows the path of least resistance, that is, the path involving minimal critical increments. Hence the atomic process referred to is not the naturally occurring one. Since, however, the chemical change as a whole is the same in the two cases, the total heat effect must be the same. The heat absorbed when two gram-molecules of hydrogen iodide decompose is 4000 cals. approximately. Applying the expression developed and tested in former papers, namely,

$$\text{heat evolved} = (E_{\text{resultants}} - E_{\text{reactants}}),$$

to the above atomic process, we obtain:

$$-4000 = E_{H_2} + E_{I_2} - 2E'_{HI}.$$

The symbol E_{I_2}, which is the critical increment of dissociation of iodine into its atoms, has the value 41,000 cals. per gram-molecule. $2 \times E'_{HI} = 2 \times 63,000$ cals. Hence the quantity E_{H_2}, which denotes the critical increment of dissociation of one gram-molecule of hydrogen into its atoms, has the value 81,000 cals. This should be sensibly identical with the heat absorbed in the dissociation of hydrogen. It is seen to be in fair agreement with Langmuir's value. The source of the discrepancy is due mainly to error in the value of E'_{HI}, which we have taken to be 63,000 cals. per gram-molecule on the basis of the rather qualitative statement

made by Berthelot and Gaudechon that hydrogen iodide is decomposed by blue or violet light. If we take the critical increment of hydrogen, in respect of dissociation into atoms, to be 87,000 cals. per gram-molecule (the value which has been employed in the compilation of the above table), it follows from a consideration of the atomic process of the decomposition of hydrogen iodide that E'_{HI} should be 66,000 cals., this being the quantity required to dissociate one gram-molecule of the substance into free atoms of hydrogen and iodine. From what has been said, this may be regarded as a more exact value of the critical increment of unimolecular decomposition than the value 63,000 cals. Certain conclusions have been drawn from this as regards the relative speeds of the unimolecular and bimolecular decompositions of hydrogen iodide in an earlier part of this paper. A further conclusion is that gaseous hydrogen iodide, when heated, should exhibit an absorption band in the region of $\nu = 7 \times 10^{14}$, or $\lambda = 429\,\mu\mu$. The author is unaware of any measurements in this connexion.

The decomposition of hydrogen iodide is particularly interesting, because it is one that is capable of occurring in two distinct ways, namely, the unimolecular and the bimolecular, and, if the previous considerations be accepted, we have fairly complete information regarding the mechanism of both. In the case of the ordinary bimolecular decomposition of hydrogen iodide, the critical increment E per gram-molecule is 22,000 cals. This is just one-third of the critical increment E', 66,000 cals., which is required for the complete dissociation of the molecule into free atoms. The ordinary bimolecular process occurs, therefore, with much greater ease, that is, at lower temperatures, than does the unimolecular process. The bimolecular process involves, therefore, a certain separation or polarisation of the atoms in the molecule, but not their complete separation. The bimolecular process may be represented in the following manner, in which an additive compound is formed:

$$2HI \longrightarrow \begin{array}{ccc} H & \text{—} & I \\ \vdots & & \vdots \\ H & \text{—} & I \end{array} \longrightarrow \begin{array}{ccc} H & \cdots & I \\ | & & | \\ H & \cdots & I \end{array} \longrightarrow H_2 + I_2.$$

The total amount of energy required to activate two gram-molecules of hydrogen iodide in this manner is 44,000 cals.

In conclusion, we may collect together the various numerical values for the critical increments of the substances dealt with in the present paper.

Substance (gaseous).	Critical increment in cals. per gram-molecule.	Reaction involving the critical increment of the previous column.
Hydrogen iodide	22,000	$2HI \rightarrow H_2 + I_2$ ordinary bimolecular reaction.
Hydrogen iodide	66,000	$HI \rightarrow H + I$ unimolecular reaction, identical with the photochemical decomposition.
Hydrogen	87,000	$H_2 \rightarrow 2H$.
Iodine	41,000	$I_2 \rightarrow 2I$.
Bromine	50 000	$Br_2 \rightarrow 2Br$.
Chlorine	86,000	$Cl_2 \rightarrow 2Cl$.

Summary.

(1) The observed rate of a unimolecular reaction is identical with the rate at which the molecules pass from the passive to the active state per second. The active state differs from the passive in respect of internal energy. The activation is ascribed to the radiation density of the absorbable radiation. In unimolecular reactions, active molecules have no real existence. They are, in fact, the resultants of the reaction. The critical increment E, that is, the quantity of energy which must be added to an average gram-molecule to raise its energy content to the critical state, is given by the expression $N_0 h\nu$, where h is Planck's constant, ν the frequency of the absorbable radiation, and N_0 the number of molecules in one gram-molecule. This statement is simply Einstein's law of the photochemical equivalent.

If the concentration of the decomposing substance is C, the provisional expression for the rate of decomposition in a unimolecular process is:

$$-dC/dt = 10^3 \cdot p \cdot C \cdot e^{-E/RT},$$

where $p = c^3/8\pi h n^3 \nu^3$, c being the velocity of light in a vacuum and n the refractive index of the system for the frequency ν. In the case of gaseous systems, $n = 1$ very nearly, and $p = 1{\cdot}6 \times 10^{56}/\nu^3$. It follows that the observed velocity constant of a unimolecular process is given by:

$$k_{\text{obs.}} = 10^3 p \cdot e^{-E/RT}.$$

Alternatively, the rate of unimolecular decomposition is given by:

$$-dC/dt = 10^3 \cdot p^2 \cdot C u_\nu,$$

where u_ν is the radiation density of the effective frequency ν, the radiation density being determined by the temperature of the system.

(2) The rate of a bimolecular reaction is identical with the

number of collisions which occur per second between the active molecules. As already pointed out in the case of *uni*molecular reactions, active molecules have no real existence. In bimolecular and multimolecular reactions generally, active molecules exist, their rate of formation being very much greater than their rate of collision, which latter term defines the observed rate of reaction. The number of active molecules in existence at any moment is proportional to the radiation density. In multimolecular reactions, the fraction of one gram-molecule existing in the active state is given on the basis of molecular statistics by the expression $e^{-E/RT}$, where E is the critical increment per gram-molecule. The fraction of one gram-molecule existing in the active state is given on the radiation basis by pu_ν, which is identical with $e^{-N_0 h\nu/RT}$ and therefore with $e^{-E/RT}$. If C is the total concentration in gram-molecules per litre, the number of active gram-molecules per litre is $C \cdot e^{-E/RT}$. The number of "effective" collisions which occur in a gaseous system between like molecules (such as molecules of hydrogen iodide) per c.c. per second is given on the molecular kinetic theory by the expression,

$$\sqrt{2} \cdot \pi \cdot u \cdot \sigma^2 \cdot (\text{number of active molecules per c.c.})^2,$$

where u is the average velocity of translation of a molecule at the temperature considered and σ is the range of approach of two molecules during a collision. At each collision between active molecules, two molecules react. Hence the rate of reaction in a bimolecular process between like molecules occurring in the gaseous state is given by:

$$-dC/dt = 5{\cdot}40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot C^2 \cdot e^{-E/RT}.$$

Alternatively, since $e^{-2E/RT} = p^2 \cdot u_\nu^2$, the rate of reaction may be written:

$$-dC/dt = 5{\cdot}40 \times 10^{21} \times u \times \sigma^2 \times p^2 \times u_\nu^2 \times C^2.$$

The observed bimolecular velocity constant, for a reaction between molecules of the same kind (expressed in gram-molecules per litre per second), is given by:

$$k_{\text{obs.}} = 5{\cdot}40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot e^{-2E/RT}$$

or

$$k_{\text{obs.}} = 5{\cdot}40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot p^2 \cdot u_\nu^2.$$

If the reaction occurs between molecules of different kinds, for example, the union of hydrogen and iodine, the velocity constant is given by:

$$k_{\text{obs.}} = 3{\cdot}8 \times 10^{21} \cdot \sigma^2 \cdot \sqrt{u_1^2 + u_2^2} \cdot e^{-(E_1+E_2)/RT}.$$

where u_1 and u_2 are the average velocities of translation of the two kinds of molecules, E_1 is the critical increment of the one kind (per gram-molecule), and E_2 is the corresponding quantity for the other kind. When the bimolecular reaction occurs between nascent atoms, all the reactants are normally in the reactive state, and therefore the exponential term reduces to unity. In such a case, for example, the combination of atoms to form the undissociated molecule of a gas, the bimolecular velocity constant is given by the expression:

$$k = 5{\cdot}40 \times 10^{21} \,.\, u \,.\, \sigma^2.$$

(3) The various statements made in (1) and (2) are borne out quantitatively in the cases examined, namely, the decomposition of hydrogen iodide (bimolecular reaction), the union of hydrogen and iodine molecules, and the dissociation of iodine, bromine, chlorine, and hydrogen gases. It is shown that the opposing velocity constants, as well as the equilibrium constants, can be calculated in regions in which, owing to the rate being either extremely great or extremely small, the chemical change cannot be determined experimentally.

(4) The velocity constant of *uni*molecular decomposition of gaseous hydrogen iodide has been calculated at various temperatures, and is shown to be negligible compared with the bimolecular constant over the range of temperature examined by Bodenstein. In the neighbourhood of 1200° abs., it is calculated that the two velocity constants should be of the same order of magnitude, and therefore the ordinary bimolecular expression should fail to apply quantitatively.

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[*Received, April 22nd*, 1918.]

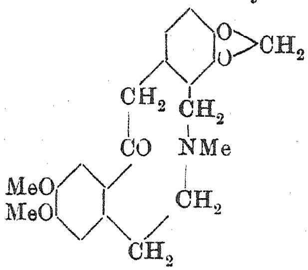
XLII.—epi*Berberine.*

By WILLIAM HENRY PERKIN, jun.

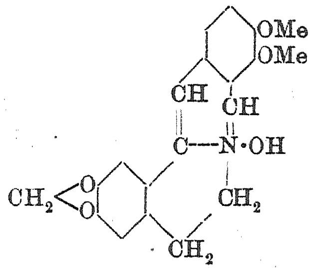
DURING the discussion of the results of an experimental investigation into the constitution of cryptopine, it was pointed out (T., 1916, **109**, 833) that the comparison of the formula of this substance with that of berberinium hydroxide* shows that these

* The nomenclature employed in this communication is clearly set out on p. 503.

substances are related in a very striking manner, and this relationship is still more clearly brought out when the formulæ of

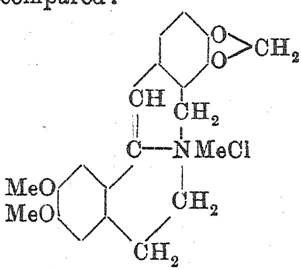


Cryptopine.

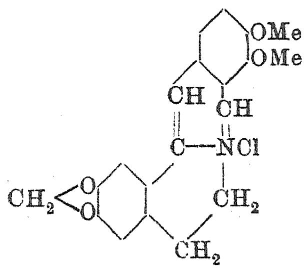


Berberinium hydroxide.

*iso*cryptopine chloride and berberinium chloride (*loc. cit.*, p. 833) are compared:



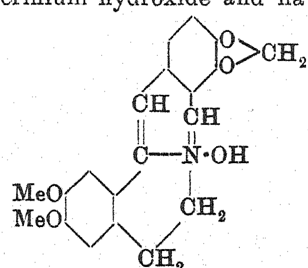
*iso*Cryptopine chloride.



Berberinium chloride.

The difference in constitution between the two alkaloids and the two salts is essentially due, first, to the presence of the *N*-methyl group in cryptopine and its absence in the berberine molecule, and, secondly, to the fact that, whereas the four oxygen atoms attached to the two benzene nuclei and carrying the methylene and the two methyl groups, are in the same position in each formula, in the case of cryptopine, the methylenedioxy-group is in the upper and the two methoxy-groups in the lower part of the molecule, whilst in berberinium hydroxide the positions are reversed.

In other words, cryptopine is related to an alkaloid isomeric with ordinary berberinium hydroxide and having the constitution



*epi*Berberinium hydroxide.

and it is this substance which has been named *epiberberinium hydroxide*. This substance has, so far, not been met with in nature, and it appeared to the author that it would be an interesting problem to endeavour to prepare it, and thus to be in a position to compare its properties and the properties of its salts with those of berberinium hydroxide and its salts. In order to obtain *epi*berberinium salts from cryptopine, it was essential, in the first place, to discover some method by which the methyl group could be detached from the nitrogen atom in the cryptopine molecule, and this proved to be an undertaking of more than ordinary difficulty.

After several unsuccessful attempts in which various condensing and oxidising agents were employed, the most hopeful course seemed to be the application of a method for removing alkyl groups from nitrogen, which had been discovered by Diels and his pupils (Diels and Fritzsche, *Ber.*, 1911, **44**, 3020; Diels and Paquin, *ibid.*, 1913, **46**, 2000). These investigators have shown that, whereas azodicarboxylic ester, $CO_2Et \cdot N{:}N \cdot CO_2Et$, combines with primary amines to yield amides, it forms additive compounds with secondary and tertiary amines which are readily hydrolysed by dilute hydrochloric acid, yielding hydrazo-ester together with aldehydes and amines. The important point is that the amines thus formed contain one radicle less than the secondary or tertiary amine employed in the first instance. Thus azodicarboxylic ester combines with dimethylamine to yield the substance,

$$CO_2Et \cdot N(CH_2 \cdot NHMe)NH \cdot CO_2Et,$$

and this is hydrolysed by dilute hydrochloric acid into hydrazodicarboxylic ester, formaldehyde, and methylamine:

$$CO_2Et \cdot N(CH_2 \cdot CHMe)NH \cdot CO_2Et + H_2O = \\ CO_2Et \cdot NH \cdot NH \cdot CO_2Et + CH_2O + NH_2Me.$$

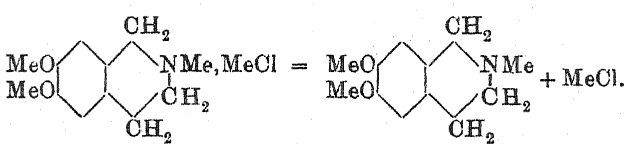
Subsequently, Diels and Ernst Fischer (*Ber.*, 1914, **47**, 2043) showed that *N*-methylpiperidine and complex substances such as atropine, morphine, and codeine could be demethylated by treatment with azodicarboxylic ester followed by hydrolysis with dilute hydrochloric acid.

As there seemed no reason why the same process might not lead to the elimination of the *N*-methyl group in cryptopine, a large number of experiments were made on the action of azodicarboxylic ester on the alkaloid under the conditions recommended by Diels and Fischer in the case of codeine and under various other conditions, including heating the substances together without dilution with a neutral solvent.

In no single case could the formation of an additive product be

observed, and most of the cryptopine was always recovered unchanged when the product of the action was boiled with dilute hydrochloric acid. It is not improbable that this negative result is due, in part at least, to the fact that cryptopine, unlike the alkaloids employed by Diels and Fischer, is very sparingly soluble in boiling acetone and other suitable solvents and also in azodicarboxylic ester, and thus intimate contact with the latter cannot be brought about.

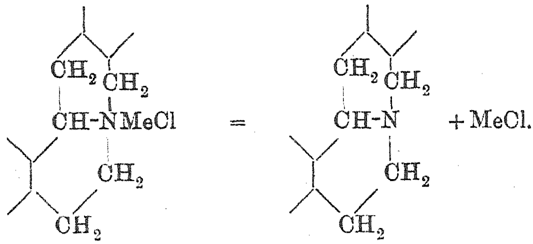
During these experiments, it was noticed that many methochlorides decompose, often at their melting points, with the evolution of gas and formation of a froth, and it was the inquiry into the meaning of this decomposition which ultimately led to the discovery of a process for preparing derivatives of *epi*berberine. One of the first substances to be investigated was 6:7-dimethoxy-2-methyltetrahydro*iso*quinoline methochloride (see below), because it happened to be available. This substance (1 gram) was placed in a test-tube, the upper part of which was drawn out to a long capillary, and the tube heated in a sulphuric acid bath, when decomposition occurred at about 270°, and, on applying a light to the end of the capillary, the issuing gas burnt with a green-edged flame and was at once recognised as methyl chloride. When effervescence had ceased, the residue was distilled under diminished pressure, and passed over as a colourless syrup which solidified to crystals melting at 83°. This substance was 6:7-dimethoxy-2-methyltetrahydro*iso*quinoline, so that decomposition had taken place according to the scheme:



In order to investigate a case approximating more closely to that of cryptopine, berberine was converted into tetrahydroanhydroberberine (tetrahydroberberine), and this into tetrahydroanhydroberberine methochloride (compare Pyman, T., 1913, **103**, 828).

The β-modification of this methochloride was heated in a drawn-out test-tube in a sulphuric acid bath exactly as described above, and again yielded methyl chloride and a dark brown syrup, but this change did not take place until the temperature had reached 285—290°. Less decomposition of the product occurred when the process was carried out under 10 mm. pressure. The residual brown mass separated from alcohol in leaflets which melted at

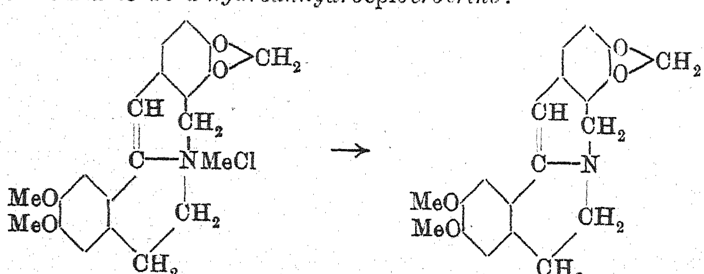
169—171°, and consisted of tetrahydroanhydroberberine, elimination of methyl chloride having occurred according to the partial scheme:



It remained now to apply this method to the quaternary chlorides derived from cryptopine, but, when this was done, great difficulties were at once encountered because of the very high temperatures which are required in order to bring about scission even under diminished pressure.

Indeed, in some of the cases investigated, the temperature necessary to cause elimination of methyl chloride is considerably above the point of decomposition of the product. In such circumstances, the isolation of any of the product is only possible when quite small quantities of material are decomposed at any one time and the experiment is rapidly carried out. The yield, even under the most favourable conditions, is then only a small one, and the preparation of any quantity of material for subsequent examination consequently a very tedious operation.

The case most exhaustively studied in the cryptopine series has been that of *iso*cryptopine chloride (T., 1916, **109**, 883), because this is by far the most accessible of the quaternary chlorides derived from this alkaloid. When *iso*cryptopine chloride, in quantities of 1 gram, is heated under diminished pressure, elimination of methyl chloride occurs at about 260°, and it has been found possible to isolate from the black residue, by employing one of the methods described on p. 506, a pure substance which on examination has been found to be *dihydroanhydro*epi*berberine*:

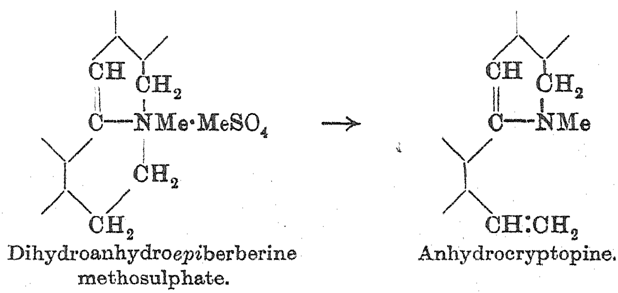


*iso*Cryptopine chloride. Dihydroanhydro*epi*berberine.

Dihydroanhydroepiberberine, $C_{20}H_{19}O_4N$, resembles dihydroanhydroberberine* in appearance and in many of its other properties. It melts at 170—172°, separates from acetone in iridescent, golden plates, and yields a very sparingly soluble hydrochloride,

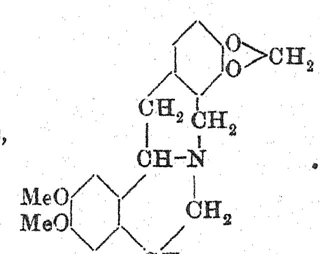
$$C_{20}H_{19}O_4N,HCl,3H_2O,$$

which crystallises in deep yellow, prismatic needles. Dihydroanhydroberberine melts at 170—172°, separates from acetone in yellow prisms, and is also characterised by the sparing solubility of its hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$, and other salts which, like the salts of dihydroanhydro*epi*berberine, are all bright yellow or orange. Dihydroanhydro*epi*berberine combines with methyl sulphate to yield the methosulphate, $C_{20}H_{19}O_4N,Me_2SO_4$, which crystallises splendidly in yellow prisms, and when boiled with methyl-alcoholic potassium hydroxide is readily decomposed with



separation of anhydrocryptopine (T., 1916, **109**, 975), a decomposition which is a welcome confirmation of the constitution assigned to dihydroanhydro*epi*berberine.

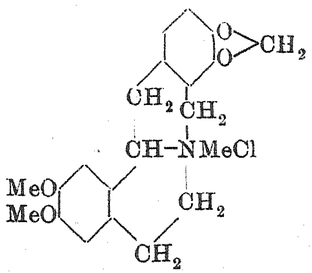
Tetrahydroanhydroepiberberine,



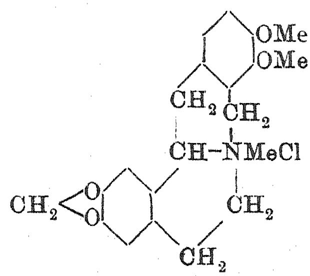
During the course of the investigation of cryptopine, $C_{21}H_{23}O_5N$, it was discovered that this alkaloid is reduced by sodium amalgam with the formation of dihydrocryptopine, $C_{21}H_{25}O_5N$, and this tertiary base, under the influence of acetyl chloride, is converted

* A detailed investigation of this substance is nearly completed, and will, it is hoped, shortly be ready for publication.

into two stereoisomeric quaternary chlorides, $C_{21}H_{24}O_4NCl$, which were named the α- and β-chlorides of *iso*dihydrocryptopine (T., 1916, **109**, 839). The close relationship between these chlorides and tetrahydroanhydroberberine methochloride was commented on



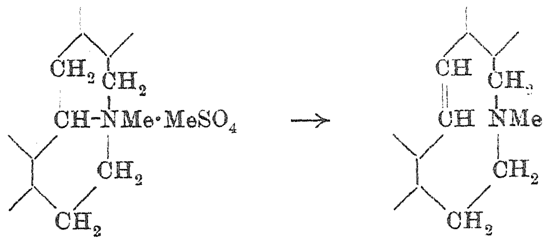
*iso*Dihydrocryptopine chloride.



Tetrahydroanhydroberberine methochloride.

at the time, as was also the fact that these substances are the counterpart of one another in all their reactions. It has already been mentioned (p. 495) that tetrahydroanhydroberberine β-methochloride is decomposed on heating with the elimination of methyl chloride and formation of tetrahydroanhydroberberine, and it therefore seemed probable that a similar decomposition would take place in the case of *iso*dihydrocryptopine chloride and result in the formation of *tetrahydroanhydro*epi*berberine.* The first experiments in this direction were disappointing, because the only chloride available was the β-modification, and this does not lose methyl chloride until nearly 300°, and then not readily, with the result that much decomposition of the product occurs. The α-modification of the methochloride is unfortunately very difficult to obtain, since it is produced only in very small quantity during the action of acetyl chloride on dihydrocryptopine. However, a small quantity of the quite pure α-chloride was prepared and found to decompose, when heated under diminished pressure, at a much lower temperature than the β-modification, namely, at about 230°, and the dark-coloured residue could then be purified by the methods given on p. 511, and yields *tetrahydroanhydro*epi*berberine.* This substance separates from alcohol in colourless needles, and not in the stout prisms so characteristic of tetrahydroanhydroberberine, but in other respects it resembles the latter in a remarkable degree. It melts at the same temperature (170—171°) and yields exactly similar, very sparingly soluble salts, of which the hydrochloride, $C_{20}H_{21}O_4N,HCl$, for example, is almost insoluble in dilute hydrochloric acid. It was subsequently found that tetrahydroanhydro*epi*berberine may be obtained from dihydroanhydro*epi*berberine by

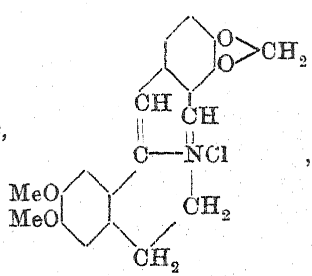
reduction with zinc or tin and hydrochloric acid, and this observation made it possible to prepare enough material for the detailed examination of this interesting substance. It is a strong base, combines readily with methyl sulphate in the cold, yielding *tetrahydroanhydro*epi*berberine methosulphate*, a colourless, crystalline substance which is decomposed by boiling with methyl-alcoholic potassium hydroxide, with the formation of anhydrodihydro-



Tetrahydroanhydro*epi*berberine methosulphate. Anhydrodihydrocryptopine. (*A*)

cryptopine (*A*) (compare T., 1916, **109**, 938).

epi*Berberinium Chloride*,

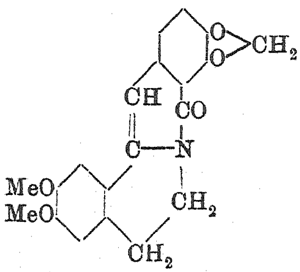


and other Salts of epi*Berberine.*

The magnificent, deep orange salts of *epi*berberine may be obtained either from dihydroanhydro*epi*berberine or tetrahydroanhydro*epi*berberine by the action of such oxidising agents as iodine or dilute nitric acid, but are best prepared from these bases by boiling with mercuric acetate in acetic acid solution, a process recommended by Gadamer (*Arch. Pharm.*, 1915, **253**, 274) in the case of the oxidation of dihydro- and tetrahydro-anhydroberberine to the corresponding berberinium salts. Thus, when dihydroanhydro*epi*berberine, dissolved in acetic acid, is boiled with mercuric acetate, mercurous acetate separates, and if this is removed by filtration and hydrochloric acid added to the filtrate, epi*berberinium chloride* separates. This salt crystallises from water in glistening, deep orange needles which are deeper in colour than the

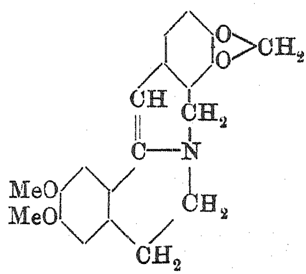
crystals of berberinium chloride, and it is remarkable that the composition of the salt, $C_{20}H_{18}O_4NCl,4H_2O$, is the same as that of berberinium chloride, and that, on heating, it behaves exactly like the latter and loses $3H_2O$ readily, but the remaining H_2O with much greater difficulty. The *sulphate*, *iodide*, and *nitrate* are also intensely coloured salts, and the picrate melts at 222°, whereas berberine picrate melts at 239—240° (Pictet and Gams, *Ber.*, 1911, **44**, 2485).

The Action of Sodium Hydroxide on epi*Berberinium Sulphate. Formation of Oxy*epi*berberine and Dihydroanhydro*epi*berberine.*



Oxy*epi*berberine.

and



Dihydroanhydro*epi*berberine.

The remarkable conversion of berberinium sulphate into a mixture of oxyberberine and dihydroanhydroberberine by the action of sodium hydroxide at the temperature of the water-bath was first observed by Gadamer (*Arch. Pharm.*, 1905, **243**, 34), and when the same process was applied to *epi*berberinium sulphate, it was found that not only did the reaction proceed in the same direction, but the conversion was even more quantitative than in the case of the berberinium salt. The dihydroanhydro*epi*berberine obtained was compared with the dihydroanhydro*epi*berberine which results from the action of heat on *iso*cryptopine chloride (p. 506), and the two preparations were found to be identical.

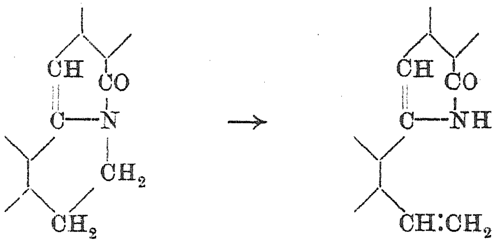
*Oxy*epi*berberine*, $C_{20}H_{17}O_5N$, melts at 240—241°, and has properties which are very similar to those of oxyberberine (m. p. 198—200°). Both are feeble bases and crystallise from acetic acid in the form of their beautifully crystalline acetates,

$$C_{20}H_{17}O_5N,C_2H_4O_2,$$

which are dissociated by water or when they are heated at 80—90° into acetic acid and oxy-berberine or -*epi*berberine.

When oxyberberine is heated in a sealed tube with dilute hydrochloric acid at 130°, it gradually undergoes isomeric change and

yields *iso*oxyberberine, the conversion taking place in the following direction:

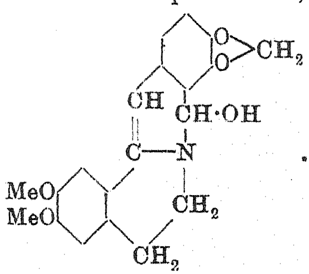


Oxyberberine. *iso*Oxyberberine.

(Perkin and Robinson, T., 1912, **101**, 262). This curious process does not take place at 130° in the case of oxy*epi*berberine, but is rapid and quantitative at about 150—160°. iso*Oxy*epi*berberine*, like the corresponding berberine derivative, is practically devoid of basic properties; it does not melt at 300°, and is even more sparingly soluble in the usual solvents than *iso*oxyberberine (m. p. 245°), but it may be recrystallised from pyridine.

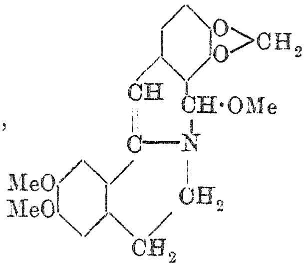
The alkaloid, berberine, $C_{20}H_{19}O_5N$, was first isolated by Gadamer (*Arch. Pharm.*, 1905, **243**, 33), who obtained it by adding a large excess of sodium hydroxide to berberinium hydroxide (or the sulphate) and extracting with ether. It crystallises from ether in yellow needles and melts at 144°.

During the course of this investigation, experiments on the action of sodium hydroxide on *epi*berberine sulphate were made under the conditions recommended by Gadamer in the hope that it might prove possible to isolate epi*berberine*,



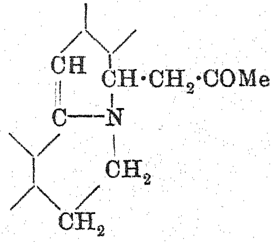
These were, however, only partly successful, since the *epi*berberine, which was obviously formed, could not be isolated in a pure condition.

The substance always contained oxy*epi*berberine, which seems to be produced as the result of oxidation even when the ethereal solution of *epi*berberine remains in contact with air. On the other hand, the *O*-methyl and *O*-ethyl derivatives have been obtained in a pure condition.

O-Methylepiberberine,  ,

and O-Ethylepiberberine.

G. M. and R. Robinson (T., 1917, **111**, 967) have recently shown that berberine is converted by treatment with methyl alcohol in the cold into *O*-methylberberine (methoxydihydroberberine), and the corresponding ethyl derivative is obtained when ethyl alcohol is employed. The present author finds that these substances are more conveniently prepared by the action of sodium methoxide or ethoxide on berberinium sulphate, and hopes shortly to publish the details of these and other experiments on several new derivatives of berberine. *O*-Methyl and *O*-ethyl derivatives of *epi*berberine are obtained under exactly similar conditions. Thus *epi*berberinium chloride (or the sulphate) yields, on treatment in methyl-alcoholic suspension with sodium methoxide, *O-methylepiberberine*, $C_{20}H_{18}O_4(OMe)N$, which separates from methylal in splendid brownish-yellow prisms and melts at 150—152°. The corresponding *O-ethyl* derivative does not crystallise so readily and melts at 135—136°. Both these substances dissolve in boiling dilute hydrochloric acid, and, on cooling, *epi*berberinium chloride separates. They also dissolve readily in boiling acetone, and when the solution is concentrated and set aside, *anhydroepiberberine-acetone*, $C_{20}H_{17}O_4N,C_3H_6O$, separates. This interesting substance, which doubtless contains the grouping



melts at 162°, crystallises in yellow prisms, and is, in appearance and properties, exactly analogous to anhydroberberine-acetone (m. p. 175°), which is similarly produced when *O*-methyl- or *O*-ethyl-berberine is dissolved in boiling acetone.

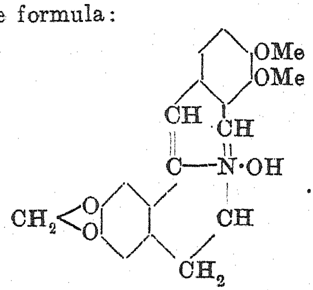
The Nomenclature of Berberine and its Salts.

During the last few years, some difficult points connected with the constitution of berberine and its salts, which still remained, have been definitely cleared up, and it seems to the author that a system of nomenclature should now be adopted which is in accordance with the new views. There can be no doubt that the alkaloid exists in two distinct modifications, one of which is crystalline and the other so far known only in solution. When a solution of the sulphate is mixed with the quantity of barium hydroxide necessary for the removal of the sulphuric acid, the filtered solution is strongly alkaline, and a similar alkaline solution is obtained when superheated steam is passed into anhydroberberine-acetone,

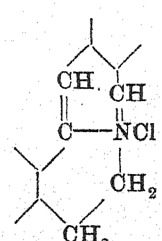
$$C_{20}H_{17}O_4N,C_3H_6O$$

(Gadamer, *Arch. Pharm.*, 1905, **243**, 33).

Unfortunately, it has not been found possible to isolate this soluble alkaline modification of the alkaloid, since decomposition occurs during evaporation even at the ordinary temperature in a vacuum desiccator, but it is now generally recognised that this alkaline solution contains the ammonium hydroxide modification represented by the formula:



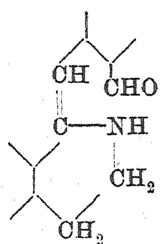
It is clear that this modification, from which the salts are obtained by the replacement of the hydroxyl group by acid radicles, may conveniently and correctly be termed *berberinium hydroxide*. The salt commonly known as berberine hydrochloride is, of course, not a hydrochloride, but a quaternary chloride containing the grouping



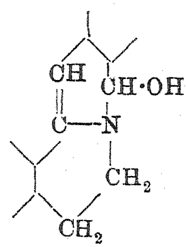
and must therefore be named *berberinium chloride*.

The solid modification of the alkaloid was first isolated by Gadamer (*loc. cit.*, p. 33), who obtained it by adding a large excess of sodium hydroxide to the aqueous solution of berberinium hydroxide, or the sulphate, and extracting with ether. It crystallises from ether in yellow needles, melts at 144°, and has the composition $C_{20}H_{19}O_5N$.

Owing to the fact that this modification yielded oxyberberine and dihydroberberine on treatment with hot concentrated sodium hydroxide solution, and therefore behaved like an aromatic aldehyde, Gadamer considered that the substance was an aldehyde of the formula I, and he therefore named it "berberinal." On the other hand, Tinkler (T., 1911, **99**, 1345) was led to the conclusion that "the evidence obtained from the spectroscopic examination of berberinal points to the fact that the substance is not the aldehydic (I), but the carbinol modification (II) of the alkaloid:



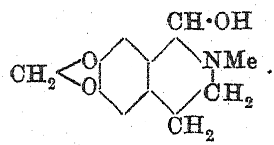
(I.)



(II.)

."

In a paper, published in 1912, on the exhaustive methylation of tetrahydroanhydroberberine (McDavid, Perkin, and Robinson, T., **101**, 1219), the carbinol formula for the alkaloid was accepted, and recently (T., 1917, **111**, 958) G. M. and R. Robinson adopted the same view, mainly as the result of a comparison of the behaviour of berberinal and cotarnine,

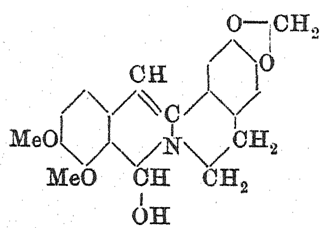


towards acetone, alcohols, amides, and other substances, with which both bases yield similarly constituted and highly characteristic condensation products. Since berberinal is obtained by the action of alkali on the salts of berberine, and on the other hand is converted into the salts of berberine by solution in acids, it appears to the author that it should, in future, be called "berberine," a plan which would do away with the anomaly

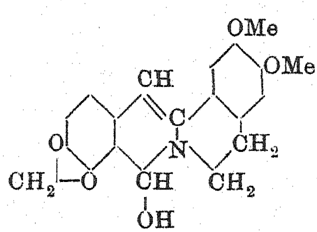
that, whereas the salts of berberine are recognised, there is, at the present time, no berberine corresponding with them. The quaternary salts of berberine, which are derived from berberinium hydroxide, should, then, be called "berberinium salts," so, for example, berberinium chloride, $C_{20}H_{18}O_4NCl$, nitrate, $C_{20}H_{18}O_4N,NO_3$, etc. The adoption of this system of nomenclature necessitates a change in the names of the reduction products derived from berberine. The substances called dihydroberberine, $C_{20}H_{19}O_4N$, and tetrahydroberberine, $C_{20}H_{21}O_4N$, are not direct reduction products of berberine, $C_{20}H_{19}O_5N$, but are derived from the alkaloid by reduction and simultaneous removal of the elements of water. Their names must therefore be altered to *dihydroanhydroberberine* and *tetrahydroanhydroberberine* respectively. Acetoneberberine, $C_{20}H_{18}(CH_2{\cdot}COMe)O_4N$, is formed from berberine by condensation with acetone, with the elimination of water, and should therefore be named anhydroberberineacetone, when its relationship to anhydrocotarnineacetone is at once recognised.

It is clear that the similar condensation products of berberine with 2-methylindole, acetophenone, *cyclo*hexanone, etc. (compare G. M. and R. Robinson, T., 1917, **111**, 959), are also anhydroberberine derivatives.

It may be pointed out that the actual placing of the berberine formulæ in the present communication has been employed in order to bring out clearly the similarity in constitution between cryptopine and berberine or *epi*berberine, but, for most purposes, there is much to be said in favour of writing the formulæ for berberine and *epi*berberine in the following manner:

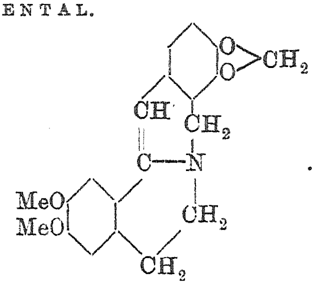


Berberine.



*epi*Berberine.

EXPERIMENTAL.

Dihydroanhydroepiberberine, .

This substance is obtained, as explained on p. 496, when *iso*cryptopine chloride is heated, and it is important that the chloride employed should be quite free from cryptopine hydrochloride, that is, that it should give no precipitate when its aqueous solution is made alkaline with ammonia and boiled.* If any cryptopine hydrochloride is present, much decomposition occurs during the heating, and the product is, of course, contaminated with cryptopine, and consequently difficult to purify.

The finely powdered and sieved chloride, after being carefully dried in the steam-oven, is placed, in quantities of not more than 2 grams, in a wide test-tube fitted with a cork and bent tube, the whole connected with a good water pump, and exhausted to, at the most, 15 mm. The test-tube, placed in a metal-bath, is gradually heated until any moisture has been removed, the temperature is then raised, rather rapidly, to 220°, during which the powder darkens in colour, and is apt to be projected about the test-tube and into the bent delivery tube.

Decomposition soon sets in, with frothing and formation of a dark brown, viscous mass, and, so soon as the disengagement of methyl chloride becomes rapid, the temperature is allowed to drop to 200—205°, and kept at this for three or four minutes and until the frothing has almost subsided. In order that the operation may be successful, the decomposition must be carried out as rapidly as possible, and the experiment requires considerable practice. The hot tube is allowed to cool slightly and then plunged into

* *iso*Cryptopine chloride, prepared by the action of phosphoryl chloride on cryptopine (T. 1916, **109**, 883) frequently contains traces of cryptopine hydrochloride. When this is the case, the whole is dissolved in boiling water, the solution made alkaline with ammonia, heated on the water-bath for some minutes and then filtered from the trace of cryptopine. The filtrate, on keeping, deposits a voluminous precipitate of pure *iso*cryptopine chloride. This quaternary salt dissolves moderately readily in boiling glacial acetic acid, and separates well as a voluminous mass of colourless groups of needles, a method which yields the salt in an exceptionally pure state.

water so that the resin may crack, become detached from the sides of the tube, and easily rubbed off with a glass rod; otherwise, if the tube is allowed to cool slowly, the resin becomes very firmly attached and is most difficult to scrape off. The crude, dark brown product may then be treated in two different ways in order to extract the dihydroanhydro*epi*berberine.

(1) The resin is dissolved in hot dilute acetic acid (25 per cent.), the dark brown solution precipitated with ammonia, the gelatinous precipitate immediately extracted with much ether, and the ethereal solution decanted or rapidly filtered from the troublesome slimy precipitate, which consists largely of unchanged *iso*cryptopine chloride. After drying over potassium carbonate, filtering, and concentrating, the ethereal solution is left in the ice-chest, when it gradually deposits a brick-red, crystalline precipitate which, after collecting and washing with ether, consists of almost pure dihydroanhydro*epi*berberine. This substance may be obtained quite pure by repeating the solution in dilute acetic acid, precipitation with ammonia, and extraction with ether, or it may be crystallised from methyl alcohol or acetone (see below).

(2) The finely powdered resin is boiled with water, which extracts unchanged *iso*cryptopine chloride and a dark reddish-brown impurity, the precipitate is collected by the aid of the pump, and washed with hot water until the filtrate is no longer red. The residue, after draining on porous porcelain, is triturated with methyl alcohol in a mortar, filtered, and the precipitate washed with methyl alcohol until the filtrate is only yellow. The ochreous residue of nearly pure dihydroanhydro*epi*berberine melts at 165—168°, and was employed in this condition for many of the experiments described in the following pages.* For analysis, the substance was recrystallised from acetone, and two analyses were made with preparations obtained by the two processes described above.

(1) 0·1072 gave 0·2793 CO_2 and 0·0564 H_2O. C=71·1; H=5·8.
0·3967 „ 14·1 c.c. N_2 at 16° and 762 mm. N=4·2.

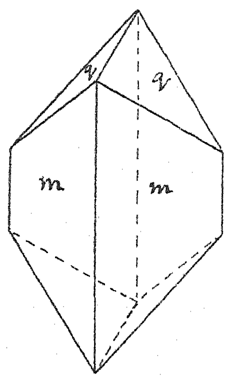
* Owing to the tedious nature of these processes and the labour required in the preparation even of a few grams of dihydroanhydro*epi*berberine, attempts have repeatedly been made to discover conditions under which larger quantities than 2 grams of *iso*cryptopine chloride could be decomposed in one operation, but without success. If, for example, 10 grams of the chloride are heated in a small flask under exactly the conditions observed in the case of the 2 grams, the decomposition appears to proceed in precisely the same way, but the product yields, at the most, traces only of pure dihydroanhydro*epi*-berberine. Apparently the time required to decompose 10 grams of *iso*-cryptopine chloride is sufficiently long to decompose the product almost entirely.

(2) 0·1179 gave 0·3075 CO_2 and 0·0615 H_2O. C=71·1; H=5·7.
$C_{20}H_{19}O_4N$ requires C=71·2; H=5·6; N=4·2 per cent.

*Dihydroanhydro*epi*berberine* melts at 172—174°, and is sparingly soluble in ether or in ethyl or methyl alcohol, even on boiling, and also in cold acetone. It is moderately soluble in boiling acetone, and separates in magnificent iridescent, golden-yellow plates resembling lead iodide, or, if the solution is allowed to cool slowly, in well-defined prisms.

The crystals, obtained from acetone, were measured by Miss M. W. Porter, and the Fedorov complex-symbol was calculated by Mr. T. V. Barker.

The crystals are monoclinic with axial ratios: $a:b:c=1·163:1:0·995$; $\beta=97°15'$. Determinations: 100/001/010. Complex-



Dihydroanhydro*epi*berberine.

symbol, 4*o*; 8/44/+4. The forms observed were *m*{110} and *q*{011}, with a prismatic habit as shown in the figure. The faces being rounded, the reflections were rather poor. Four crystals were measured and the results obtained are placed in the following table.

Face.	No. of readings.	Azimuth (ϕ). Limits.	Obs	Calc	Polar distance (ρ). Limits	Obs.	Calc
m(110)	11	40°39′—41°13′	*40°56′	—	90° 0′—90° 9′	90°0′	90° 0′
q(011)	4	6 42 — 7 52	*7 7	—	44 56—45 15	*45 5	—

*Dihydroanhydro*epi*berberine* dissolves readily in acetic acid to a deep yellow solution, and the base is not precipitated by dilution with water, but separates on the addition of ammonia as a caseous precipitate which, on warming, becomes crystalline. If a trace of the base, dissolved in a drop of acetic acid, is mixed with sulphuric

acid, there is at first little change, but, on keeping, the solution becomes cherry-red.

*Salts of Dihydroanhydro*epi*berberine.*

Hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$.—When dihydroanhydro-*epi*berberine is moistened with hydrochloric acid, it is converted into a yellow powder of the hydrochloride which, whilst very sparingly soluble in cold water, and particularly so in cold dilute hydrochloric acid, dissolves in much boiling water and separates in groups of flat, yellow, prismatic needles. This brilliant orange salt loses its water of crystallisation and becomes brick-red in the steam-oven, but on exposure to the air, it gradually absorbs moisture and becomes yellow again:

0·1319, air-dried salt, lost 0·0157 at 100°. $H_2O = 11·9$.

0·1048, dried at 100°, gave 0·2470 CO_2 and 0·0490 H_2O. C = 64·2; H = 5·2.

$C_{20}H_{19}O_4N,HCl,3H_2O$ requires $H_2O = 12·6$ per cent., and the anhydrous salt requires C = 64·2; H = 5·3 per cent.

Hydrobromide.—The addition of boiling dilute potassium bromide to the boiling solution of the hydrochloride gives a brick-red precipitate which consists of groups of striated prismatic needles. For analysis, it was dried at 100°:

0·0810 gave 0·1705 CO_2 and 0·0343 H_2O. C = 57·4; H = 4·7.

$C_{20}H_{19}O_4N,HBr$ requires C = 57·4, H = 4·8 per cent.

*Dihydroanhydro*epi*berberine Methosulphate*, $C_{20}H_{19}O_4N,Me_2SO_4$. —This derivative is best prepared by sealing up the finely divided base (1 gram) with freshly distilled methyl sulphate (1·5 c.c.) in a small tube and shaking vigorously from time to time. There is no evolution of heat on mixing, and combination takes place only very gradually, but is complete in about eight days. The product is triturated with benzene, the yellow mass collected by the aid of the pump, washed with benzene, and recrystallised from methyl alcohol, in which it is sparingly soluble. The prisms which separate on gradual cooling are unfortunately so striated as to be unsuitable for measurement, and the substance also becomes opaque when exposed to the air.

After remaining exposed to the air for eight days, the substance lost only 3·1 per cent. at 100°, and on analysis:

0·1013 gave 0·2115 CO_2 and 0·0531 H_2O. C = 56·9; H = 5·8.

$C_{20}H_{19}O_4N,Me_2SO_4$ requires C = 57·0; H = 5·4 per cent.

*Dihydroanhydro*epi*berberine methosulphate* darkens above 250°

and melts rather sharply at 260° with vigorous decomposition to a black froth. The deep yellow prisms from methyl alcohol become pale yellow on stirring with water, dissolve very sparingly in the cold, but much more freely on boiling, and the solution gelatinises if rapidly cooled. The aqueous solution gives no precipitate with ammonia, and rapidly reduces permanganate even at −5°.

This methosulphate is sparingly soluble in glacial acetic acid, and the addition of sulphuric acid produces, at first, no coloration, then a pale green gradually develops; on keeping, the solution becomes purplish-black, and the addition of a drop of dilute nitric acid changes the colour to intense purple and then to brown. When the finely divided methosulphate is mixed with methyl-alcoholic potassium hydroxide (15 per cent.), it dissolves, but, on boiling, the solution clouds and a pale yellow precipitate separates. This was collected, washed with methyl alcohol, then with water, and dissolved in boiling methyl alcohol, when, on rubbing, minute yellow prisms immediately separated which melted at 108—110°, and consisted of anhydrocryptopine (p. 497).

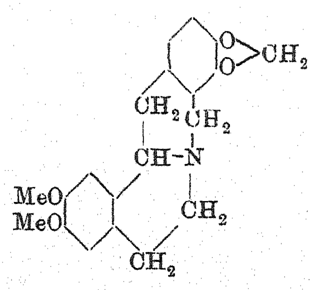
*Dihydroanhydro*epi*berberine methiodide*, $C_{20}H_{19}O_4N,MeI$, is obtained as an immediate, very sparingly soluble, ochreous precipitate when potassium iodide is added to the saturated aqueous solution of the methosulphate, but if the solutions are sufficiently dilute and are mixed boiling, a clear solution may be obtained, from which the iodide separates as a fluffy precipitate consisting of microscopic groups of needles:

0·1135 gave 0·2176 CO_2 and 0·0487 H_2O. C=52·3; H=4·7.

$C_{20}H_{19}O_4N,MeI$ requires C=52·6; H=4·6 per cent.

This methiodide darkens and softens at about 230°, and then melts and decomposes at about 245° to a deep red syrup.

*Tetrahydroanhydro*epi*berberine*,



This substance is most readily obtained by the action of heat on *iso*dihydrocryptopine α-chloride (T., 1916, **109**, 935), but it may also be prepared by the action of heat on the corresponding β-chloride (*loc. cit.*, p. 934). In the case of the α-chloride, the

decomposition is conveniently carried out by heating quantities of not more than 2 grams of the pure dry salt in a test-tube, drawn out to a long capillary, by means of a sulphuric acid bath. At about 270° effervescence sets in, due to the escape of methyl chloride, which may be ignited at the end of the capillary and burns with a green-edged flame.

As soon as the frothing has ceased, the tube is taken out of the bath and left to cool, when the brown syrup will have solidified and the dark product may be purified by crystallisation from boiling alcohol, from which nearly pure tetrahydroanhydro*epi*berberine separates at once in pale brown needles. An alternative method is to convert the crude product into the very sparingly soluble hydrochloride (see below), to purify this by crystallisation from acetic acid, and, after decomposing the colourless salt with dilute alkali, to crystallise the base from much alcohol.

In the case of the β-chloride, decomposition does not proceed so smoothly, owing no doubt to the fact that this chloride fuses with much greater difficulty than the α-chloride. The elimination of methyl chloride is best carried out with quantities of not more than 2 grams in a test-tube heated in a metal-bath under the conditions described in detail in the case of the preparation of dihydroanhydro*epi*berberine from *iso*cryptopine chloride (p. 506). The decomposition of the β-chloride does not begin much below 300°, and should not be pushed to completion, otherwise the product will be very dark coloured and difficult to purify. Purification is best effected by converting the dark resin into the sparingly soluble hydrochloride, crystallising this from acetic acid until it is quite colourless, and then regenerating the base and crystallising this from much alcohol.

*Preparation of Tetrahydroanhydro*epi*berberine by the Reduction of Dihydroanhydro*epi*berberine.*—In the event of the α- or β-chlorides of *iso*dihydrocryptopine not being available, this method is probably the most convenient for the preparation of the tetrahydro-base. Crude dihydroanhydro*epi*berberine (p. 507) is dissolved in hot concentrated hydrochloric acid, the solution diluted with an equal volume of water, and boiled with a large excess of granulated tin for several hours. The product, diluted with much water, is freed from tin by means of hydrogen sulphide in the usual manner, the filtrate from the tin sulphide is concentrated and left for several days, during which the sparingly soluble hydrochloride of tetrahydroanhydro*epi*berberine separates. This is collected, recrystallised, decomposed by alkali, and the base crystallised from much alcohol. Two different specimens gave the following results on analysis:

0·1015 gave 0·2625 CO_2 and 0·0569 H_2O. C=70·5; H=6·2.
0·1021 " 0·2652 CO_2 " 0·0575 H_2O. C=70·8; H=6·3.
0·3965 " 14·1 c.c. N_2 at 15° and 758 mm. N=4·2.
$C_{20}H_{21}O_4N$ requires C=70·8; H=6·2; N=4·2 per cent.

*Tetrahydroanhydro*epi*berberine* melts at 170—171° and is sparingly soluble in boiling methyl alcohol, but somewhat more readily so in boiling ethyl alcohol, from both of which it separates in colourless needles. It is sparingly soluble in cold acetone, moderately readily so on boiling, and crystallises on slowly cooling in prisms; boiling benzene dissolves the base freely, and, on cooling, it separates in prismatic needles. In purifying specimens of the base, which are highly coloured, acetone is the best solvent. Tetrahydroanhydro*epi*berberine does not exhibit the tendency so marked in the case of tetrahydroanhydroberberine of separating from solvents in stout, well-developed prisms, and unfortunately all attempts to obtain it in a state suitable for measurement have so far been unsuccessful. The solution of a crystal in a drop of acetic acid gives at first no coloration on the addition of sulphuric acid, but gradually a violent tint develops.

*Salts of Tetrahydroanhydro*epi*berberine.*

Hydrochloride, $C_{20}H_{21}O_4N,HCl$.—The finely powdered base is immediately converted by moistening with dilute hydrochloric acid into the sparingly soluble hydrochloride, which separates from much boiling water in microscopic bundles of needles like fern fronds:

0·1140 gave 0·2687 CO_2 and 0·0608 H_2O. C=64·3; H=5·9.
$C_{20}H_{21}O_4N,HCl$ requires C=64·0; H=5·8 per cent.

In its properties, this hydrochloride resembles the sparingly soluble hydrochloride of tetrahydroanhydroberberine, but it appears to be even less readily soluble than the latter in dilute hydrochloric acid, and must be classed as one of the least readily soluble of alkaloid hydrochlorides. When it is heated in a capillary tube, the upper surface in contact with air begins to darken at 195—200°, and becomes orange-red, whilst the remainder is scarcely discoloured; at 285—290°, the whole melts with vigorous effervescence to an orange-red froth. Highly coloured specimens of the hydrochloride are readily obtained colourless by recrystallisation from glacial acetic acid, in which the salt is sparingly soluble and from which it separates in colourless nodules or circular, warty groups, the colouring matter remaining almost entirely in the mother liquor.

The *sulphate* is much more readily soluble than the hydrochloride, and separates either as a jelly or as a voluminous mass of bent and striated needles. When the aqueous solution of this salt is boiled, a very sparingly soluble sulphate gradually separates as a sandy powder.

The *nitrate* separates, on the addition of dilute nitric acid, to the hot solution of the sulphate, as a very sparingly soluble, crystalline powder.

*Tetrahydroanhydro*epi*berberine Methosulphate and its Conversion into Anhydrodihydrocryptopine* (A and B).—When tetrahydroanhydro*epi*berberine (3 grams) is mixed with freshly distilled methyl sulphate (4 c.c.), the mixture becomes very warm, liquefies, and then sets to a stiff paste of the methosulphate, which may be freed from the excess of methyl sulphate by washing with benzene and then be crystallised from methyl alcohol. A more convenient method of preparation is to dissolve the base (2 grams) in boiling benzene (10 c.c.), and, after cooling until crystallisation just commences, to add freshly distilled methyl sulphate (3 c.c.).

The clear solution soon begins to deposit the methosulphate as a hard crust, which is collected, washed with benzene, and crystallised from methyl alcohol. An air-dried specimen of the needle-shaped modification of the substance which separates from water (see below) appears to have the formula $C_{20}H_{21}O_4N,Me_2SO_4,3H_2O$:

0·7220, air-dried salt, lost 0·0834 at 100°. $H_2O=11·5$.

0·1201, dried at 100°, gave 0·2486 CO_2 and 0·0635 H_2O. $C=56·5$; $H=5·9$.

$C_{20}H_{21}O_4N,Me_2SO_4,3H_2O$ requires $H_2O=10·4$ per cent., and the anhydrous substance requires $C=56·7$, $H=5·9$ per cent.

*Tetrahydroanhydro*epi*berberine methosulphate* melts and decomposes at about 255—260°; it is sparingly soluble in cold methyl alcohol, but readily so on boiling, and separates in large, colourless prisms. It is sparingly soluble in cold water, but dissolves readily on boiling, and the solution either sets to a jelly or deposits the substance in groups of hairs. At some concentrations, the methosulphate is deposited in groups of striated prisms; the liquid then becomes filled with glistening needles, and when warmed the needles dissolve and the prisms remain. It is therefore probably dimorphous.

The hot dilute aqueous solution of the methosulphate gives, on the addition of boiling dilute potassium iodide, a clear solution, from which the iodide separates as a voluminous mass of fine hairs. This substance is *iso*dihydrocryptopine *α*-iodide, since it melts at

acetic acid (30 c.c. of 25 per cent.), adding a solution of mercuric acetate prepared from 4·5 grams of mercuric oxide, and, after remaining over night, heating on the steam-bath for half an hour. The product is worked up exactly in the way explained in detail in the case of the corresponding oxidation of tetrahydroanhydro-*epi*berberine (see above), and yields about 2 grams of pure *epi*berberinium chloride (see analysis 2).

epi*Berberinium chloride*, $C_{20}H_{18}O_4NCl,4H_2O$, separates from water, in which it is comparatively readily soluble, in brilliant orange needles, which when dry have a striking, satiny lustre. It is much less readily soluble in dilute hydrochloric acid than in water, and is best crystallised by adding concentrated hydrochloric acid to the moderately concentrated aqueous solution. It is very sparingly soluble in boiling methyl alcohol, but separates beautifully in striated, orange needles; on the other hand, it dissolves readily in hot glacial acetic acid, and crystallises well from this solvent. When the glistening, orange needles of the chloride are moistened with methyl alcohol, they lose their lustre and become an opaque chrome-yellow powder, a change doubtless due to the loss of the water of crystallisation:

(1) 0·1136, air-dried salt, lost 0·0139 in the steam-bath at about 90°. $H_2O=12·2$.

0·0997 then gave 0·2273 CO_2 and 0·0472 H_2O. C = 62·1; H = 5·2.

(2) 0·1073 dried at about 90° gave 0·2437 CO_2 and 0·0491 H_2O. C = 61·9; H = 5·1.

$C_{20}H_{18}O_4NCl,4H_2O$ losing $3H_2O=12·17$ per cent.

$C_{20}H_{18}O_4NCl,H_2O$ requires C = 61·6; H = 5·1 per cent.

In an experiment in which the salt had been heated in an air-bath at 100—105°, it had darkened somewhat and gave C = 63·7, H = 4·8, whereas $C_{20}H_{18}O_4NCl$ requires C = 64·6, H = 4·8 per cent. The salt was therefore practically anhydrous.

The *platinichloride* separates as a bright orange-red precipitate when platinic chloride is added to the warm solution of *epi*berberinium chloride in dilute hydrochloric acid:

0·1148 gave 0·1878 CO_2 and 0·0351 H_2O. C = 44·6; H = 3·4.

$(C_{20}H_{18}O_4NCl)_2PtCl_4$ requires C = 44·4; H = 3·3 per cent.

epi*Berberinium sulphate* is obtained when hot dilute sulphuric acid is added to a concentrated solution of the chloride as a bright yellow salt which crystallises in needles.

The characteristic *picrate* separates as an orange, amorphous precipitate when picric acid is added to a hot dilute solution of the chloride. It melts not very sharply at 222° with decomposition, and is very sparingly soluble even in much boiling water. It is also

very sparingly soluble in boiling alcohol, in which it dissolves to the extent of about 1 gram in a litre, and, on cooling, separates almost completely in flat, microscopic needles melting at 222°.

Action of Sodium Hydroxide on epi*Berberinium Sulphate. Formation of* epi*Berberine* (epi*Berberinal*), *Oxy*epi*berberine, and Dihydroanhydro*epi*berberine* (compare p. 500).

In the introduction to this communication (p. 501), it is explained that berberine (berberinal) is readily obtained by treating berberinium sulphate with concentrated aqueous sodium hydroxide and extracting with ether (Gadamer, *Arch. Pharm.*, 1905, **243**, 34), but this process has not been found so successful in the case of *epi*berberinium sulphate. The best result is obtained when an excess of sodium hydroxide (50 per cent.) is added to a solution of *epi*berberinium sulphate (5 grams) in 500 c.c. of freshly boiled water. The ochreous precipitate which separates is rather sparingly soluble in ether, and the filtered ethereal solution begins almost immediately to deposit needles of oxy*epi*berberine (see below). If, however, the ochreous precipitate is immediately collected in an atmosphere of coal gas, it is almost completely soluble in dilute hydrochloric acid with the formation of *epi*berberinium chloride, and yields, on analysis, numbers agreeing approximately with those required for the formula of *epi*berberine:

0·1090 gave 0·2693 CO_2 and 0·0540 H_2O. C=67·4; H=5·4.

$C_{20}H_{19}O_5N$ requires C=68·0; H=5·4 per cent.

Oxidation takes place rapidly when the moist substance is left in contact with air, and in the course of a few hours a considerable portion will be insoluble in dilute hydrochloric acid and consist of oxy*epi*berberine.

Completely satisfactory results were obtained in investigating the conversion of *epi*berberinium sulphate into oxy*epi*berberine and dihydroanhydro*epi*berberine by the action of concentrated sodium hydroxide. This decomposition is analogous to that described in the case of the action of sodium hydroxide on berberinium sulphate (compare Gadamer, *loc. cit.*, pp. 35 and 36).

The sulphate (3 grams) is thoroughly mixed with sodium hydroxide (12 c.c. of 20 per cent.), the flask containing the mixture placed in cold water, and the water gradually raised to the boiling point and kept at this temperature for an hour. The product, which is not so dark-coloured as in the case of the corresponding experiment with berberinium sulphate, is diluted with much water, filtered by the aid of the pump, the ochreous powder washed and

then warmed with excess of very dilute hydrochloric acid, when dihydroanhydro*epi*berberine dissolves and a pale ochreous mass with a satiny lustre remains, which consists of nearly pure oxy*epi*berberine. This was thoroughly washed, dried in the steam-oven, dissolved in a little glacial acetic acid, and allowed to remain in a closed test-tube, when deep yellow needles of *oxy*epi*berberine acetate* separated. This was collected, washed with acetic acid, and dried between filter paper:

0·1368 gave 0·3221 CO_2 and 0·0641 H_2O. C = 64·2; H = 5·2.

$C_{20}H_{17}O_5N,C_2H_4O_2$ requires C = 64·2; H = 5·1 per cent.

On exposure to moist air, this acetate gradually becomes opaque, owing to loss of acetic acid, and oxy*epi*berberine remains. The acetate is readily soluble in acetic acid, and if the solution is mixed with two volumes of boiling water, the clear liquid soon becomes filled with needles of oxy*epi*berberine. When the acetate is heated in a capillary tube, it becomes paler at about 110° and melts at 238—240°, the atmosphere of acetic acid having no effect on the melting point, which is that of oxy*epi*berberine. The acetate is quantitatively decomposed at 90—95° into acetic acid and oxy*epi*berberine, as the following experiment shows:

1·2052 lost at 90—95° 0·1736. $C_2H_4O_2$ = 14·4.

$C_{20}H_{17}O_5N,C_2H_4O_2$ requires $C_2H_4O_2$ = 14·6 per cent.

The residue of pure *oxy*epi*berberine* was analysed:

0·1260 gave 0·3145 CO_2 and 0·0557 H_2O. C = 68·1; H = 4·9.

$C_{20}H_{17}O_5N$ requires C = 68·3; H = 4·8 per cent.

*Oxy*epi*berberine* gradually darkens above 210° and melts approximately at 240—241° to a dark brown syrup. It is very sparingly soluble even in boiling alcohol, and separates in well-developed rhombic plates, the angle of the rhomb being 66°; in polarised light, diagonal extinction.

*Dihydroanhydro*epi*berberine*.—The hot dilute hydrochloric acid filtrate which had been separated from the oxy*epi*berberine, as explained above, was mixed with more hydrochloric acid and left in the ice-chest, when it deposited a voluminous mass of slender, orange needles. This salt was collected, recrystallised from dilute hydrochloric acid, dissolved in hot water, and rendered alkaline with ammonia, when a milky liquid resulted which was extracted with much ether. After rapidly drying over potassium carbonate and concentrating, striated, lemon-yellow prisms separated, on keeping, which melted at 172°, and consisted of dihydroanhydro*epi*berberine (Found: C = 71·0; H = 5·7. $C_{20}H_{19}O_4N$ requires C = 71·2; H = 5·6 per cent. Compare p. 508).

iso*Oxyepiberberine* (compare p. 501).

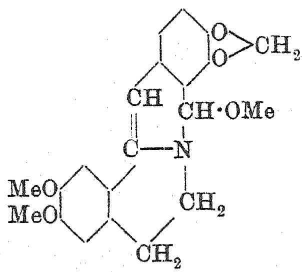
The conversion of oxyberberine into *iso*oxyberberine takes place gradually when the former is heated with dilute hydrochloric acid at 130° (Bland, Perkin, and Robinson, T., 1912, **101**, 264), but recent experiments have shown that the change occurs much more readily and completely when a temperature of 150—160° is employed.

In attempting to convert oxy*epi*berberine into *iso*oxy*epi*-berberine, the conditions originally employed in the case of the corresponding conversion of oxyberberine into *iso*oxyberberine were adhered to, and the temperature was kept at 130° for five hours, but, on working up the contents of the sealed tube, practically the whole of the oxy*epi*berberine was recovered unchanged. Some slight action had taken place, because, on opening the tube, the liquid on the sides of the walls became coloured purple by the action of the air. When, however, the experiment was repeated at 150—160° for six hours, complete transformation had taken place. The contents of the tube were filtered by the aid of the pump, the residue washed and boiled out with glacial acetic acid, in which *iso*oxy*epi*berberine is very sparingly soluble. The ochreous mass was then dissolved in boiling pyridine and filtered, when the substance separated as a voluminous mass of microscopic needles. It was collected, washed with hot methyl alcohol, and dried at 100°:

0·0984 gave 0·2473 CO_2 and 0·0448 H_2O. C=68·5; H=5·0.
$C_{20}H_{17}O_5N$ requires C=68·4; H=4·8 per cent.

*iso*Oxy*epi*berberine scarcely darkens at 270°, but gradually blackens at 300° without melting. It is almost insoluble in the usual solvents, including boiling glacial acetic acid, in which the isomeric *iso*oxyberberine is comparatively readily soluble. A trace of the substance, rubbed on the sides of a test-tube, is coloured violet by sulphuric acid and dissolves to a pale brown solution; in the case of a similar experiment with nitric acid, the substance is coloured violet and dissolves to a deep bluish-violet solution, which becomes permanganate colour on the addition of water. When the suspension of the substance in alcohol is mixed with ferric chloride and warmed, a green colour develops. A very delicate reaction is obtained by dissolving a trace of *iso*oxy*epi*berberine in boiling glacial acetic acid, cooling, and adding an equal volume of sulphuric acid. The addition of a drop of dilute nitric acid to the pale yellow solution produces a most intense violet coloration, and this, on dilution with water, becomes magenta. *iso*Oxy-

berberine is insoluble in aqueous or alcoholic alkali even on boiling (compare *loc. cit.*, p. 264), but *iso*oxy*epi*berberine is coloured deep brown by methyl-alcoholic potassium hydroxide, and dissolves, on warming, to a brown solution, from which a crystalline substance—probably a potassium salt—separates. On the addition of water, a brown solution is produced, from which acids liberate a flocculent precipitate. It appears, therefore, that *iso*oxy*epi*berberine is more readily hydrolysed than is *iso*oxyberberine. The addition of benzenediazonium chloride to the brown alkaline solution in aqueous alcohol gives, at first, a rather feeble brownish-red colour, but, on warming, this becomes very intense.

O-*Methyl*epi*berberine*, ,

O-*Ethyl*epi*berberine, and Anhydro*epi*berberine-acetone.*

O-Methyl*epi*berberine is readily prepared from *epi*berberinium chloride or sulphate, either by the action of methyl-alcoholic potassium hydroxide or of sodium methoxide, and of these the latter is to be preferred.

(1) *epi*Berberinium chloride loses its brilliant colour when it is mixed with methyl-alcoholic potassium hydroxide (10 per cent.), and a pale drab, crystalline precipitate separates, especially on warming gently.

This was collected, washed with methyl alcohol, then with water, and again with methyl alcohol, and found to consist of practically pure *O*-methyl*epi*berberine. For the analysis given below, a little of it was rapidly recrystallised from methylal, from which it separated in yellowish-brown prisms.

(2) The best method for preparing the *O*-methyl derivative is the following: *epi*Berberinium chloride (2 grams), suspended in methyl alcohol, is heated on the steam-bath, sodium (1 gram) dissolved in methyl alcohol added, and the whole rapidly filtered. Crystallisation begins at once, and pure *O*-methyl*epi*berberine separates in a most beautiful manner in glistening, old-gold prisms. After remaining until cold, these were collected and washed with methyl alcohol.

The following analyses were made with specimens obtained from each of the above methods of preparation:

(1) 0·1088 gave 0·2723 CO_2 and 0·0570 H_2O. C=68·3; H=5·8.
(2) 0·1111 „ 0·2798 CO_2 „ 0·0582 H_2O. C=68·7; H=5·8.
$C_{21}H_{21}O_5N$ requires C=68·6; H=5·7 per cent.

O-*Methyl*epi*berberine* melts at about 150—152° with decomposition to a black froth. Attempts to recrystallise it with the object more particularly of obtaining crystals suitable for measurement and comparison with *O*-methylberberine were unsuccessful. This is mainly due to the fact that the substance undergoes decomposition on boiling with such solvents as methylal or methyl alcohol, and a substance separates which melts at about 230—240°, and was readily identified as oxy*epi*berberine (p. 518). *O*-Methyl*epi*berberine is immediately converted by dilute hydrochloric acid into a deep orange-red salt which crystallises from dilute hydrochloric acid in brilliant orange needles, gives no precipitate when ammonia is added to its aqueous solution, and consists of *epi*berberinium chloride.

O-*Ethyl*epi*berberine*, $C_{20}H_{18}(OEt)O_4N$, is prepared in a similar manner to the *O*-methyl derivative by boiling *epi*berberinium chloride with alcohol, adding excess of sodium ethoxide, and immediately filtering by the aid of the pump, when, on keeping in the ice-chest, circular, crystalline masses soon begin to form. After twenty-four hours, these were collected, washed first with alcohol, then with water, and dried at 80°:

0·1109 gave 0·2808 CO_2 and 0·0598 H_2O. C=69·1; H=6·0.
$C_{22}H_{23}O_5N$ requires C=69·3; H=6·0 per cent.

O-*Ethyl*epi*berberine* melts and decomposes at about 135—136°, and is sparingly soluble in boiling alcohol, from which it separates in groups of striated needles. It is apparently not so readily converted into oxy*epi*berberine as the corresponding *O*-methyl derivative. It dissolves readily in boiling dilute hydrochloric acid, and *epi*berberinium chloride separates on cooling.

*Anhydro*epi*berberine-acetone*, $C_{20}H_{18}(CH_2\cdot COMe)O_4N$. — *O*-Methyl*epi*berberine dissolves readily in boiling acetone, and, if the solution is concentrated and set aside, a crust of yellow prisms of anhydro*epi*berberine-acetone gradually separates, but this substance does not crystallise with the same facility nor is it so highly characteristic as anhydroberberine-acetone. After recrystallisation from acetone, the substance melted not very sharply at about 162° and gave the following results on analysis:

0·1107 gave 0·2846 CO_2 and 0·0586 H_2O. C=70·1; H=5·9.
$C_{23}H_{23}O_5N$ requires C=70·2; H=5·9 per cent.

The author wishes to state that the cost of the material required for this investigation was partly defrayed by a grant from the Royal Society Research Fund.

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[*Received, May 4th*, 1918.]

XLIII.—*Water-in-oil Emulsions.*

By ALFRED ULRICH MAX SCHLAEPFER.

WITH a system consisting of two liquid phases, A and B, it is theoretically possible to obtain two classes of emulsions, namely, A-in-B emulsions, in which A is the disperse phase and B the medium, and B-in-A emulsions, in which B is the interior and A the exterior phase (compare Wo. Ostwald, *Kolloid Zeitsch.*, 1910, **6**. 103).

At first, the power of producing emulsions was exclusively attributed to substances which, when dissolved in one of the liquid phases, reduce the tension on their interface, thus facilitating the dispersion of one of them in the other.

Pickering (T., 1907, **91**, 2001) was the first to prove that it is possible to obtain emulsions of hydrocarbon oils in water by means of solid emulsifiers, such as precipitates of basic copper sulphate, basic iron sulphate, etc., which are insoluble in either liquid and are moistened more by water than by the oil. He showed that the finely divided particles of the emulsifier form a coat over the oil droplets, preventing their coalescence. The action of the particles of hydrophile colloids, such as soap, etc., which had long been known as excellent emulsifiers, he considered to be similar to that of the grains of basic copper sulphate.

Pickering showed also that the type of an emulsion is largely independent of the proportions in which the two phases are present when he prepared emulsions of kerosene (disperse phase) in dilute soap solution (medium) containing up to 99 per cent. of kerosene in a 1 per cent. soap solution. Such emulsions, in which the disperse phase is greatly in excess over the medium, show an extremely high viscosity. Pickering did not consider the possibility of making emulsions of water in oil.

As Bancroft (*J. Physical Chem.*, 1912, **16**, 475) pointed out in his discussion of Pickering's results, it is to be expected as their

corollary that insoluble particles, which are more easily moistened by oil than by water, will have a tendency to facilitate the emulsification of water in oil. In other words, if the solid particles of the emulsifiers have a lower surface tension with the phase *A* than with the phase *B*, it is to be expected that an emulsion will be formed with *A* as medium and *B* as disperse phase, and vice versa.

Newman (*J. Physical Chem.*, 1914, **18**, 34) found that soaps of certain alkaline earths, especially those containing magnesium, were excellent emulsifiers for emulsions of water in benzene. He showed also that mixed paints which contain a certain amount of water are to be considered as emulsions of the water-in-oil type. He drew the conclusion that in the latter case the emulsifying properties are to be ascribed to rosin and not to the pigment.

The experiments described below are concerned with the preparation of water-in-oil emulsions with the aid of a finely divided solid insoluble in both liquids, which is more easily wetted by the oil than by the water phase.

EXPERIMENTAL.

Materials Used.

Kerosene.—A water-white kerosene fraction (D^{15} 0·785) was redistilled over sodium. Distillation by Redwood's method gave the following result:

Distillate per cent.	0	10	20	30	40	50	60	70	80	90	95
Boiling point	156°	158°	160°	161°	166°	170°	174°	176°	182°	192°	208°

Carbon.—Best American carbon black (gas black, soot) was extracted for two days with hot benzene.

The distilled water was obtained from a tinned copper still.

The following experiments were carried out with these materials.

Experiment 1.—Thirty c.c. of water, 70 c.c. of kerosene, and 1 gram of carbon were shaken together in a flask. In this way, an emulsion was obtained which contained water as the disperse phase. This could easily be shown on a watch-glass by the fact that the emulsion mixed freely with kerosene, but not with water. Under a microscope, it was found that the droplets of water were covered with a dark brown skin of adsorbed particles of carbon. Those particles which were not adsorbed formed aggregates in the kerosene phase. The emulsion was liquid. After remaining for one day, it separated into pure kerosene, floating on the top, and a viscid emulsion which was still of the water-in-kerosene type and was stable for several weeks.

Experiment 2.—Seventy c.c. of water, 30 c.c. of kerosene, and

1 gram of carbon were shaken in a flask. In this, as in the other experiments here described, it was immaterial whether the carbon was added first to the water or to the oil or to both when mixed. The emulsion mixed freely with kerosene but not with water, and was therefore again of the water-in-oil type. It was so viscid that it did not flow out of a reversed test-tube. It kept for more than a week without altering.

To show the influence of the quantitative proportions of the two phases more clearly, experiments were made in order to determine the time of flow of the emulsions from a 5 c.c. pipette. For the same pipette (all experiments were carried out at about 18°), water required on an average 3·3 seconds and the kerosene 3·5 seconds. The results of these experiments are shown in the table on p. 525.

In this case, the emulsions were prepared in the manner recommended by Pickering, by alternately filling and emptying a garden syringe. The number of strokes, which is a crude criterion of the amount of mixing, has a certain influence on the viscosity of the mixture. The table clearly shows the enormous increase of viscosity which is produced by an increasing proportion of the inner phase.

In experiments 7 and 8, it was not possible to get all the water into the emulsion. It is worth special notice that neither in these nor in any other similar experiments was it ever possible to obtain an emulsion of kerosene in water with the aid of carbon. When the amount of water was too large to be carried by the kerosene, an emulsion with less water was formed, together with an unaltered residuum of water. Since the size of droplets occurring together changed within a large range, especially in the emulsions containing a large amount of water, it does not seem justifiable to make any speculations on the fact that the limit of stability under the described conditions was about 70 per cent. water-content (compare Wo. Ostwald, *loc. cit.*). More water could be added by stirring, but in consequence of the considerable tension on the interface of the two liquids, the droplets stirred in were large. It might, of course, be possible to obtain emulsions of higher water-concentration with carbon black if a fourth compound were added to lower the surface tension between the two liquid phases.

Similar emulsions could be made in an analogous way, using turpentine, benzene, toluene, etc., instead of kerosene.

It may be stated that carron oil, the well-known liniment for burns which is prepared with lime-water and linseed or rape oil, is an emulsion of the water-in-oil type, whilst embrocations are well known to be of the oil-in-water type.

Carron oil mixes freely with organic solvents, but not with water

No of Expt.	Quantities used.			Time required for emulsion to flow out of 5 c.c. pipette* (Means of 6 experiments each)			Amount of kerosene in c.c. floating on top of 100 c.c. of emulsion after twenty-four hours.	Percentage of water in residual emulsion after twenty-four hours.	REMARKS.
	Kerosene, c.c.	Water, c.c.	Carbon, grams.	After 160 strokes with syringe.	After 320 strokes with syringe.	After 480 strokes with syringe.			
3	240	60	1·5	4·4	4·7	5·3	48	38·5	Diameter of droplets 0·001—0·02 mm.
4	180	120	1·5	7·4	7·8	—	not measured	—	—
5	120	180	1·5	—	26	44	11	67·5	—
6	90	210	1·5	Did not flow out of pipette or from reversed test-tube.			none	—	Diameter of droplets 0·001—0·1 mm.
7	60	240	1·5	Emulsified part did not flow out of pipette or a reversed test-tube.					It was not possible to emulsify all the water in the experiments. An emulsion of water in kerosene was obtained besides pure water. No emulsion of kerosene in water could be obtained.
8	60	240	3·0						

* As marks, the 5 c.c. mark on the upper tube and the beginning of the lower tube at the bottom of the bulb were taken.

without shaking, and easily dissolves oil colours, but not dyes soluble in water.

Summary.

(1) It is possible to make emulsions of water as disperse phase in organic solvents with the aid of finely divided carbon as emulsifier.

(2) The carbon particles, without leaving the oil phase, form a skin over the water droplets, preventing their coalescence.

(3) The order in which the ingredients are added does not make any difference to the final product.

(4) The emulsions obtained in this way are the more viscous the more water they contain.

(5) Carron oil is a water-in-oil emulsion.

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[*Received, May* 16*th*, 1918.]

XLIV.—*The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. The Influence of certain Inorganic Haloids on the Optical Rotatory Powers of α-Hydroxy-acids, α-Amino-acids, and their Derivatives.*

By GEORGE WILLIAM CLOUGH.

The Walden Inversion.

THE discovery of the phenomenon known as the Walden inversion was made in connexion with transformations of certain derivatives of succinic acid, and it therefore seemed possible that the change of configuration was due either to the presence of an atom of hydrogen attached to the asymmetric carbon atom or to the fact that the optically active compounds in question were carboxylic acids. Although the configurative change may be due to one or both of these causes in certain cases, it has been shown that a Walden inversion can be effected in a compound containing a tertiary asymmetric carbon atom (McKenzie and Clough, T., 1910, **97**, 1016), and also in compounds which do not contain a carboxyl

group. In his studies on this phenomenon, Fischer observed that the action of a reagent on an ester frequently yielded a compound of the enantiomorphous configuration to that of the compound produced by the same reagent on the corresponding acid, and in such examples he assumed that the action on the ester was not accompanied by change of configuration. That an inversion is possible in the case of an ester has been shown by the fact that phosphorus pentachloride and thionyl chloride yield chloro-esters of opposite signs when they react with the same optically active ethyl α-phenyl-lactate (McKenzie and Clough, T., 1910, **97**, 2564). Further, it is not necessary that the optically active compound should contain either a carboxyl or carbalkyloxy-group, for it has been found possible to effect the interconversion of the optically active phenylmethylcarbinols (T., 1913, **103**, 687).

Several attempts have been made to decide in which reactions an inversion occurs by employing certain assumptions regarding the mechanism of the reactions in question (Armstrong, T., 1896, **69**, 1399; Gadamer, *Chem. Zeit.*, 1910, **34**, 1004; 1912, **36**, 1327; Biilmann, *Annalen*, 1911, **388**, 338). It has been shown that Biilmann's hypothesis cannot be applied to all the examples which have been investigated (McKenzie and Clough, *loc. cit.*); and, moreover, Senter and Drew's experiments (T., 1916, **109**, 1091) concerning the influence of the solvent on the rotatory sign of the phenylaminoacetic acids produced by the action of ammonia on the active phenylchloroacetic acids emphasise the difficulty of drawing conclusions regarding the specific action of a reagent from considerations of the probable mechanism of the reactions. It may still be said that "there does not exist at the present time any criterion whereby the relation between the configuration of an optically active compound and that of a derivative from it can be decisively ascertained" (Frankland, T., 1913, **103**, 738).

Accordingly, it seemed desirable that the problem should be investigated by an entirely different method. The present author has therefore made experiments with the object of ascertaining whether the measurements of the rotatory powers of similarly constituted compounds would reveal regularities between the rotatory values and the relative configurations of the active compounds. In such an investigation, it is necessary to consider the influence of the conditions (temperature, solvent, and concentration) on the rotatory powers of each compound, and also to study the relative effects of substituents introduced into the groups attached to the asymmetric carbon atom. It would, indeed, be impossible to draw a sharp distinction between these two methods of procedure if the assumption is made that some solvents form labile compounds

with the active solute (compare Walden, *Ber.*, 1905, **38**, 408). When it is also recalled that the work of Pickard and Kenyon has brought to light surprising regularities when the rotations of derivatives from a given compound are measured for light of different wave-lengths, it is evident that an entirely satisfactory comparison of the optical rotatory powers of two parent compounds can be made only when the rotatory powers of the compounds and their derivatives have been measured under many varying conditions. Fortunately, the labours of Frankland, Guye, Purdie, Patterson, Walden, and others have resulted in the accumulation of much data available for a comparison of the rotatory powers of the common optically active aliphatic α-hydroxy-acids, whilst the publications of Fischer contain rotation constants for the majority of the active α-amino-acids. The measurements made by the author are by no means as comprehensive as could be wished, but it appears desirable to place on record the results which have been obtained for several α-hydroxy- and α-amino-acids, and to discuss these from the above point of view, especially as conclusions have been drawn concerning the relative configurations of compounds of the sugar series from a consideration of their rotatory powers (Hudson, *J. Amer. Chem. Soc.*, 1917, **39**, 462). In the present paper, attention is directed particularly to regularities observed in the effect of temperature and of certain inorganic haloids on the optical rotatory powers of some α-hydroxy- and α-amino-acids and esters in aqueous or methyl-alcoholic solution.

α-Hydroxy-acids and their Derivatives.

In previous communications (T., 1914, **105**, 49; 1915, **107**, 96, 1509), it has been established that the optical rotatory powers of configuratively similar hydroxy-derivatives of succinic acid containing a carboxyl or carbalkyloxy-group are influenced in the same sense by the presence of the haloids of the alkali or alkaline earth metals in aqueous solutions. These salts diminish considerably the numerical values for the specific rotatory powers and frequently reverse the sign of rotation. With the view of ascertaining whether other hydroxy-acids and esters are, in this respect, similar to malic and tartaric acids, the author has examined the rotatory powers of *l*-lactic acid, methyl *l*-lactate, and *d*-glyceric acid in aqueous solution and in aqueous solutions of certain neutral salts. It is well known that *l*-lactic acid, which is lævorotatory in aqueous solution, yields dextrorotatory salts and esters. The lævorotatory power of this acid in aqueous solution diminishes with rise of temperature, and is ultimately reversed. The influence of temperature on the

optical rotatory power of *l*-lactic acid in aqueous solution is thus similar to that on methyl *l*-lactate in the homogeneous condition, for Patterson and Forsyth observed that rise of temperature increases the dextrorotatory power of this ester (T., 1913, **103**, 2263). The presence of sodium or barium haloids increases the lævorotatory power of *l*-lactic acid (table I), and similarly the dextrorotatory power of methyl *l*-lactate in aqueous solution is diminished or reversed by the salts employed (table II). The rotatory values being usually small, the measurements recorded are for mercury-green light ($\lambda = 5461$).

TABLE I.

The Influence of Sodium Chloride, Sodium Bromide, and Barium Bromide on the Optical Rotatory Power of l-*Lactic Acid* in Aqueous Solution.*

Salt.	Grams of salt added to 25 c.c. of solution.	p.	d^{15}.	$\alpha^{15}_{gr.}$ ($l=4$).	$[\alpha]^{15}_{gr.}$
None	—	10·73	1·027	− 0·95°	− 2·2°
Sodium chloride	5·85	8·71	1·162	− 3·08	− 7·6
Sodium bromide	10·30	7·65	1·293	− 3·16	− 8·0
Barium bromide	14·80	6·79	1·485	− 7·10	− 17·7

* This specimen contained 8 per cent. of *d*-lactic acid.

TABLE II.

The Influence of Inorganic Salts on the Optical Rotatory Power of Methyl l-*Lactate* in Aqueous Solution.*

Solvent.	p.	d^{20}.	$\alpha^{20}_{gr.}$ ($l=2$).	$[\alpha]^{20}_{gr.}$
None	100	1·093	+ 18·34°	+ 8·4°
Water	10·0	1·012	+ 0·29	+ 1·4
Aqueous sodium chloride (*N*)	10·0	1·050	+ 0·11	+ 0·5
,, ,, ,, (4-*N*)	10·37	1·150	− 0·50	− 2·1
,, sodium bromide (*N*)	10·0	1·080	+ 0·10	+ 0·5
,, potassium chloride (*N*)	10·0	1·054	+ 0·10	+ 0·5
,, ammonium chloride (*N*)	10·0	1·027	+ 0·19	+ 0·9
,, calcium chloride (*N*)	10·0	1·054	− 0·22	− 1·0
,, barium chloride (*N*)	10·0	1·094	− 0·28	− 1·3
,, barium bromide (4-*N*)	9·81	1·456	− 2·60	− 9·1

* This specimen contained 5 per cent. of methyl *d*-lactate.

Notwithstanding the fact that the influence of water on the rotatory power of methyl *l*-lactate is opposite in sense to that of this solvent on the esters of *d*-malic acid or *d*-tartaric acid, it is obvious that the changes of rotation caused by the inorganic haloids are the same in character for *l*-lactic acid and methyl *l*-lactate as

for the configuratively similar compounds *d*-tartaric acid and methyl *d*-tartrate. On the other hand, the changes observed in the case of *d*-glyceric acid are opposite in character to those for *l*-lactic acid. Frankland and Frew have shown that *d*-glyceric acid is dextrorotatory in aqueous solution at the ordinary temperature, but that the specific rotation $[\alpha]_D$ becomes zero in dilute solution (T., 1891, **59**, 96); moreover, this acid yields lævorotatory salts and esters (T., 1893, **63**, 297, 511, 1410). The author finds that *d*-glyceric acid in aqueous solution becomes lævorotatory on raising the temperature, and that the addition of certain inorganic haloids increases the rotation of the acid (table III).

TABLE III.

The Influence of Sodium Chloride and Barium Chloride on the Optical Rotatory Power of d-*Glyceric Acid in Aqueous Solution.*

Salt.	Grams of salt added to 25 c.c. of solution.	p.	d^{20}.	$\alpha^{20}_{gr.} (l=2)$.	$[\alpha]^{20}_{gr.}$.
None	—	2·40	1·01	$\pm$ 0·00°	$\pm$ 0·0°
Sodium chloride	5·85	1·84	1·17	+ 0·21	+ 4·9
Barium chloride	5·20	1·90	1·22	+ 0·32	+ 6·9

The earlier experiments of Stubbs (T., 1911, **99**, 2265), Patterson and Anderson (T., 1912, **101**, 1833), and the present author concerning the influence of neutral salts on the optical rotatory powers of certain compounds in solution were made with aqueous solutions. Patterson and Anderson, however, found that the dissolution of certain salts in homogeneous ethyl tartrate depressed the rotation of this ester. Walden observed that ethyl tartrate (α_D^{15} +6·1°, $l=1$), after saturation with hydrogen bromide, gave α_D^{15} −7·0° ($l=1$) (*Ber.*, 1905, **38**, 407). It has now been found that the dissolution of about 5 per cent. of calcium chloride in methyl *l*-lactate depresses the rotation from $\alpha^{15}_{gr.}$ +8·55° to $\alpha^{15}_{gr.}$ +5·5° ($l=1$). In this connexion, it should be stated that a solution of calcium chloride in this ester readily deposits a crystalline *compound* of the formula $CaCl_2,4C_4H_8O_3$ (Found: Cl = 13·4. Calc.: Cl = 13·5 per cent.). A similar compound of calcium chloride with ethyl lactate has been described by Strecker (*Annalen*, 1854, **91**, 355). Measurements of the rotatory powers of several compounds dissolved in methyl alcohol and in methyl alcohol containing sodium bromide show that the effect of this salt is even greater in methyl alcohol than in water (table IV).

TABLE IV.

The Influence of Sodium Bromide on the Optical Rotatory Powers of l-*Malic Acid*, d-*Tartaric Acid*, *Methyl* l-*Lactate*, *Methyl* l-*Malate*, *and Methyl* d-*Tartrate in Methyl-alcoholic Solution.*

Compound.	$[\alpha]^{15}_{gr.}$ (in methyl alcohol, $c=10$).	$[\alpha]^{15}_{gr.}$ (in methyl-alcoholic sodium bromide, N, $c=10$).
l-Malic acid	$-5{\cdot}9°$	$+21{\cdot}8°$
d-Tartaric acid	$+2{\cdot}6$	$-9{\cdot}0$
Methyl *l*-lactate	$+5{\cdot}4$	$-5{\cdot}8$
Methyl *l*-malate	$-9{\cdot}4$	$+9{\cdot}1$
Methyl *d*-tartrate	$+2{\cdot}7$	$-12{\cdot}6$

It is of interest to note that sodium bromide exerts a distinct influence on the rotatory powers of the methyl and ethyl esters of *d*-diacetoxysuccinic acid in methyl-alcoholic solution, but the effect observed is opposite in character to that of the same salt on the corresponding esters of *d*-tartaric acid. Methyl *d*-diacetoxysuccinate gave $[\alpha]^{15}_{gr.}$ $-18{\cdot}3°$ in methyl alcohol ($c=4$), whilst in N-methyl-alcoholic sodium bromide the value was $[\alpha]^{15}_{gr.}$ $-12{\cdot}2°$ ($c=4$); similarly, for ethyl *d*-diacetoxysuccinate the values obtained were $[\alpha]^{15}_{gr.}$ $+3{\cdot}6°$ ($c=5$) and $[\alpha]^{15}_{gr.}$ $+7{\cdot}6°$ ($c=5$) respectively. It thus appears that the specific effect of salts on the optical rotatory powers of hydroxy-acids and esters is due to the presence of alkylic hydroxyl groups in these compounds.

Now, Freudenberg (*Ber.*, 1914, **47**, 2037) has shown that the four hydroxy-acids, *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid, all possess the same relative configurations, that is to say, the hydrogen atoms, the hydroxyl and carboxyl groups attached to the asymmetric carbon atoms have a similar spatial disposition in the molecules of these compounds. These relationships have been proved by transformations which do not involve replacements of groups directly attached to the asymmetric carbon atom, and inasmuch as no example is known in which such a change produces inversion, it is justifiable to assume that no configurative change occurs in these reactions. When the rotatory powers of these four acids and of their derivatives are compared, the regularities observed are extremely striking and significant, especially when it is remembered that malic and tartaric acids are dibasic (and may thus be regarded also as β-hydroxy-acids), and that tartaric acid contains two adjacent asymmetric carbon atoms. It has been shown by the author that the influence of temperature on the rotatory powers of these related acids* in aqueous solution

* *l*-Malic acid was examined, but the discussion is simplified by reference to *d*-malic acid.

is similar in character for the four compounds, the dextrorotation being increased (or the lævorotation diminished) in each case. The rotations are also increased by dilution, and the molecular rotations of the sodium or potassium salts in aqueous solution are in each case higher (that is, more positive) than those of the free acids in aqueous solution. Further, the presence of inorganic haloids influences the rotatory powers of the acids in aqueous solution in the same sense.

Similar regularities are observed on examination of the rotatory values of the esters of these acids. Thus the temperature–rotation curves for methyl *l*-lactate (Patterson and Forsyth, *loc. cit.*), methyl *l*-glycerate (Frankland and McGregor, T., 1894, **65**, 768), methyl *d*-malate (Clough, T., 1915, **107**, 103), and methyl *d*-tartrate (Pictet, *Jahresber.*, 1882, 855) are all similar in character. The molecular rotations of the esters, which are higher than those of the parent acids (calculated, where possible, by extrapolation), increase, in the case of the lower members of the homologous series, with increase of molecular weight. The influence of a given solvent on the rotations of esters of the configuratively related acids, *d*-tartaric acid, *d*-malic acid, and *l*-lactic acid, is in general the same in character, the elevating effect of aromatic nitro-compounds and the depressing effect of aliphatic halogen compounds being particularly striking. It must be stated that there are a few important exceptions to this rule. The regularities observed when inorganic salts are dissolved in solutions of esters of the acids in question are well illustrated by table IV. It therefore appears that, in general, changes of the same character are brought about in the optical rotatory powers of the similarly con-

TABLE V.

The Influence of Substituents on the Molecular Rotations $[M]_D$ *of* l-*Lactic Acid*, l-*Glyceric Acid*, d-*Malic Acid, and* d-*Tartaric Acid.*

	Y = H.	Y = Me.	Y = Et.
l-$CH_3 \cdot CH(OH) \cdot CO_2Y$	− 2° (H_2O, c = 5)	+ 8·6°	+ 12·2°
l-$CH_2(OH) \cdot CH(OH) \cdot CO_2Y$	− 2·3 (H_2O, c = 20)	+ 5·8	+ 12·3
d-$CO_2Y \cdot CH_2 \cdot CH(OH) \cdot CO_2Y$ ...	− 6·3*	+ 11·1	+ 19·8
d-$CO_2Y \cdot (CH \cdot OH)_2 \cdot CO_2Y$	− 4·2*	+ 3·8	+ 15·9

	X = Ac, Y = Et.	X = Bz, Y = Me.	X = Me, Y = Me.
l-$CH_3 \cdot CH(OX) \cdot CO_2Y$	+ 79·7°	− 59·0°	+ 112·7°
l-$CH_2(OX) \cdot CH(OX) \cdot CO_2Y$	+ 35·6	− 89·2	+ 103·5
d-$CO_2Y \cdot CH_2 \cdot CH(OX) \cdot CO_2Y$	+ 52·3	+ 11·4	+ 92·4
d-$CO_2Y \cdot (CH \cdot OX)_2 \cdot CO_2Y$	+ 10·0	− 123·6	+ 180·0

* By extrapolation, Winther, *Zeitsch. physikal. Chem.*, 1902, **41**, 181; or other references, see Frankland and Gebhard, T., 1905, **87**, 865.

stituted optically active α-hydroxy-acids possessing the same relative configurations by similar alterations of temperature, by dissolution in a given solvent, or by the addition of a given optically inactive substance to solutions of the active compounds. Further, it is evident from table V that the introduction of a given radicle into the molecules of the configuratively similar hydroxy-acids in question usually produces alterations of the same character in the rotatory powers.

It should now be possible to determine the relative configurations of similar α-hydroxy-acids with reference to *d*-tartaric acid, but unfortunately in no case are the available data so comprehensive as in the above examples. A comparison of the values for derivatives from *l*-α-hydroxybutyric acid (Guye and Jordan, *Compt. rend.*, 1895, **120**, 1274) with those in table V indicates that *l*-α-hydroxybutyric acid possesses a configuration similar to that of *l*-tartaric acid.

		X=H, Y= NH_4.	X=H, Y= Et.	X=H, Y= *iso*Bu.	X=Ac, Y= *iso*Bu.	X=Bz, Y= *iso*Bu.
l-$C_2H_5 \cdot CH(OX) \cdot CO_2Y$	$[M]_D$	$-16.8°$ (H_2O)	$-2.5°$	$-12.3°$	$-62.0°$	$+3.2°$

The author has examined the influence of sodium chloride (or bromide) on *d*-β-phenyl-lactic acid and its methyl ester (table VI) with results which, taken in conjunction with those in table IV, show that this acid is related configuratively to *d*-tartaric acid.

TABLE VI.

The Influence of Sodium Haloids on the Optical Rotatory Powers of d-β-*Phenyl-lactic Acid and Methyl* d-β-*Phenyl-lactate in Solution.*

Compound.	Solvent.	c.	t.	$\alpha^t_{gr.}$ (l=2).	$[\alpha]^t_{gr.}$
d-β-Phenyl-lactic acid ...	Water	2·505	20°	+ 1·28°	+ 25·5°
,, ,, ,, ...	Aqueous sodium chloride (4*N*)	0·665	20	+ 0·18	+ 13·5
,, ,, ,, ...	Methyl alcohol	10·0	20	+ 4·20	+ 21·0
,, ,, ,, ...	Methyl-alcoholic sodium bromide (*N*)	10·0	20	− 0·41	− 2·0
Methyl *d*-β-phenyl-lactate	Methyl alcohol...	10·0	18	− 0·90	− 4·5
,, ,, ,,	Methyl-alcoholic sodium bromide (*N*)	10·0	18	− 4·46	− 22·3

The values for *l*-α-hydroxy*iso*hexoic acid calculated from the results of Scheibler and Wheeler (*Ber.*, 1911, **44**, 2684) are $[M]^{20}_D$ −13·7° (in water) and $[M]^{20}_D$ −36·7° (in *N*-sodium hydroxide), whilst the ethyl ester gives $[M]^{20}_D$ −18·3°. Fischer and Moreschi (*Ber.*, 1912, **45**, 2447) find that *l*-α-hydroxyglutaric acid is feebly

lævorotatory in aqueous solution at 18°, and that the sodium salt gives $[M]_D^{20}$ $-14{\cdot}6°$. On the other hand, whilst *l*-α-hydroxy*iso*-valeric acid is slightly lævorotatory in aqueous solution, the zinc salt in *N*-sodium hydroxide gives $[M]_D^{20}$ $+35{\cdot}4°$ (Fischer and Scheibler, *Ber.*, 1908, **41**, 2891). It thus seems very probable that *l*-α-hydroxy*iso*valeric acid possesses the same configuration as *d*-tartaric acid, but that *l*-α-hydroxy*iso*hexoic acid and *l*-α-hydroxy-glutaric acid are enantiomorphously related to this acid. The conclusion is therefore drawn that *l*-lactic acid,* *l*-glyceric acid, *d*-malic acid, *d*-α-hydroxybutyric acid, *l*-α-hydroxy*iso*valeric acid, *d*-α-hydr-oxy*iso*hexoic acid, *d*-α-hydroxyglutaric acid, and *d*-β-phenyl-lactic acid all possess the same relative configurations as *d*-tartaric acid. These optically active acids will be referred to in the sequel as "*d*"- and their optical antipodes as "*l*"-aliphatic α-hydroxy-acids.

The remarkable effect on rotatory power which has been frequently noticed when a phenyl group is attached to the asymmetric carbon atom rendered it advisable to compare the influence of salts on the rotatory power of such a compound with that exerted on aliphatic compounds. Sodium chloride was found to increase the lævorotatory power of *l*-mandelic acid in aqueous solution from $[\alpha]_{gr.}^{14}$ $-188°$ $(c=1{\cdot}6)$ to $[\alpha]_{gr.}^{14}$ $-203°$ (4*N*-sodium chloride, $c=1{\cdot}6$), and sodium bromide had a similar effect on ethyl *l*-mandelate, which gave $[\alpha]_{gr.}^{15}$ $-141°$ in methyl alcohol $(c=10)$ and $[\alpha]_{gr.}^{15}$ $-181°$ in *N*-methyl-alcoholic sodium bromide $(c=10)$. If the rules which have been established from a study of the simple aliphatic α-hydroxy-acids may be applied when a phenyl group is attached to the central carbon atom, it would follow that *l*-mandelic acid is related to *d*-tartaric acid. This conclusion receives support on reference to the rotations of some derivatives (esters, amide) from *l*-mandelic acid. The lævorotatory power of *l*-mandelic acid in aqueous solution diminishes on dilution, and the salts possess numerically lower molecular rotations than the free acid in aqueous solution. The lævorotatory powers of the acid in aqueous solution (Lewkowitsch, *Ber.*, 1883, **16**, 1567) and of the esters in the pure condition (J. W. Walker, *J. Physical Chem.*, 1909, **13**, 574) diminish with rise of temperature, and the molecular rotatory powers of the esters decrease numerically with increase of molecular weight—methyl ester $[M]_D^{20}$ $-276°$, ethyl ester $[M]_D^{20}$ $-226°$ (J. W. Walker, *loc. cit.*), *iso*butyl ester $[M]_D^{20}$ $-209°$ (Walden, *Zeitsch. physikal. Chem.*, 1895, **17**, 706). In all these respects, the behaviour of l-mandelic acid is opposite to that of *l*-malic acid.

* In this paper, the designations (*d*- or *l*-) of the optically active compounds mentioned are those usually given in the literature, and are not used to indicate the relative configurations of the compounds.

It must be repeated that the employment of this method cannot be regarded as wholly satisfactory unless the compounds and their derivatives are examined in a systematic manner under varying conditions, but it is shown later that there is confirmatory evidence that the conclusions which have been drawn with regard to the configurations of the active aliphatic α-hydroxy-acids are in all probability correct. It may be recalled that Frankland and Turnbull have shown the configurative relationships of the optically active esters of αβ-dichloropropionic acid by investigating the effect of temperature on their rotatory powers (T., 1914, **105**, 456), and that the present author has discussed the relative configurations of the optically active normal secondary alcohols on the basis of their optical rotation constants determined by Pickard and Kenyon (P., 1913, **29**, 357. Compare Kenyon, T., 1914, **105**, 2232). Pickard and Kenyon have suggested the employment of a "characteristic diagram" (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, [*A*], **88**, 388) for determining whether a change of configuration has taken place in the formation of a derivative (P., 1913, **29**, 296).

α-Amino-acids and their Derivatives.

The author has previously shown that the optical rotatory powers of *l*-asparagine and *l*-aspartic acid are very susceptible to the influence of inorganic salts (T., 1915, **107**, 1509). Pfeiffer subsequently obtained similar results for *d*-alanine, the dextrorotatory power of which in aqueous solution is raised by the dissolution of lithium chloride or calcium chloride; thus, the addition of 5 grams of calcium chloride to 10 c.c. of an aqueous solution of *d*-alanine (10 per cent.) raised $[\alpha]_D$ from $+2{\cdot}10°$ to $+11{\cdot}85°$ (*Ber.*, 1915, **48**, 1938). For the sake of comparison with *l*-aspartic acid, the present author has determined the rotations of *d*-alanine in aqueous solutions of other salts (table VII).

TABLE VII.

The Influence of Inorganic Salts on the Optical Rotatory Power of d-*Alanine in Aqueous Solution.*

Solvent.	c	$\alpha^{15}_{gr.}(l=2)$.	$[\alpha]^{15}_{gr.}$
Water	10·0	+0·58°	+2·9°
Aqueous potassium chloride (N)	10·0	0·61	3·0
" sodium chloride (N)	10·0	0·66	3·3
" barium chloride (N)	10·0	0·70	3·5
" barium bromide ($4N$)	10·0	0·96	4·8
" hydrogen chloride (1·5 mols.)	5·78	2·06	17·8

Inasmuch as these results are similar to those observed for *l*-aspartic acid, which is dextrorotatory in aqueous solution at the

ordinary temperature, but becomes lævorotatory at higher temperatures, the influence of temperature on the rotatory power of *d*-alanine in aqueous solution has been studied and found to be quite similar to that on *l*-aspartic acid, a reversal in the sign of rotation being realised at about 70°.

The investigation has been extended to *d*-glutamic acid. The optical behaviour of this compound is parallel to that of *l*-aspartic acid; both these compounds are dextrorotatory in aqueous solution at the ordinary temperature, and elevation of temperature depresses the rotatory values, but whereas *l*-aspartic acid becomes lævorotatory at about 60°, it was not found possible to reverse the rotatory sign of *d*-glutamic acid in aqueous solution. The presence of neutral or acid salts in solution increases the dextrorotatory power of *d*-glutamic acid (table VIII).

TABLE VIII.

The Influence of Inorganic Salts on the Optical Rotatory Power of d-*Glutamic Acid in Aqueous Solution.*

Solvent.	p.	d^{25}.	$a^{25}_{\text{gr.}}(l=4)$.	$[a]^{25}_{\text{gr.}}$.
Water	1·50	1·003	+ 0·80°	+ 13·3°
Aqueous sodium chloride (N)	1·50	1·043	0·90	14·4
,, ,, ,, ($4N$)	1·51	1·152	1·10	15·8
,, potassium chloride (N)	1·53	1·050	0·95	14·8
,, barium chloride (N)	1·53	1·092	0·96	14·4
,, barium bromide ($4N$)	1·51	1·500	1·64	18·1
,, sodium hydroxide (1 mol.)	12·25	1·075	− 1·88	− 3·6
,, ,, ,, (2 mols.)	6·55	1·050	+ 3·22	+ 11·7
,, hydrogen chloride (1·5 mols.)	8·75			+ 37·4

A comparison of the rotatory powers of hydroxy-acids with those of their esters in the presence of neutral salts having shown that both classes of compounds are influenced in a similar manner, it was advisable to examine polarimetrically an ester of an amino-acid under various conditions, especially as such an examination might possibly throw some light on the constitution of amino-acids in aqueous solution. Accordingly, ethyl *l*-aspartate has been examined in various solvents. The lævorotatory power of this ester is increased by rise of temperature and reversed by dissolution in water or hydrochloric acid. The gradual addition of water (with which the ester is completely miscible) at first causes a rapid diminution of the lævorotation until $p=80$, when the solution is dextrorotatory; further dilution after $p=50$ has very little influence on the specific rotation. The addition of sodium or barium haloids increases the dextrorotatory power of the ester in aqueous solution, and sodium bromide reverses the lævorotatory power of the ester in methyl-alcoholic solution at 20°.

TABLE IX.

The Influence of Solvents on the Optical Rotatory Power of Ethyl l-*Aspartate.*

Solvent.	c.	$\alpha^{15}_{gr.}(l = 2)$.	$[\alpha]^{15}_{gr.}$.
None		$-6{\cdot}34°$ ($l = 0{\cdot}5$)	$-11{\cdot}7°$
Benzene	10·92°	$-2{\cdot}75$	$-12{\cdot}6$
Chloroform	11·02	$-2{\cdot}13$	$-9{\cdot}7$
Acetone*	20·0	$-3{\cdot}50$	$-8{\cdot}8$
Water	21·7	$+1{\cdot}83$	$+4{\cdot}2$
Water	12·25	1·03	4·2
Aqueous sodium chloride ($4N$)	10·81	1·44	6·7
Aqueous barium bromide ($4N$)	14·50	3·34	11·5
,, calcium chloride ($5N$)	13·21	3·84	14·5
,, hydrogen chloride (N)	11·37	2·73	12·0
Methyl alcohol	20·0	$\alpha^{20}_{gr.} - 0{\cdot}19$	$[\alpha]^{20}_{gr.} - 0{\cdot}5$
Methyl-alcoholic sodium bromide (N)	20·0	$\alpha^{20}_{gr.} + 1{\cdot}72$	$[\alpha]^{20}_{gr.} + 4{\cdot}3$

* Ethyl *l*-aspartate reacts with acetone, the rotation changing from $\alpha_{gr.} - 3{\cdot}50°$ to $\alpha_{gr.} - 56{\cdot}6°$ ($c = 20$) in fifteen hours.

Finally, measurements made with benzoyl-*d*-alanine show that when the amino-group is displaced by the benzoylamino-group, the characteristic optical behaviour of the amino-acid disappears. For example, although benzoyl-*d*-alanine is only feebly dextrorotatory in aqueous solution ($[\alpha]^{15}_{gr.} + 0{\cdot}3°$, $p = 12$), little alteration could be detected on raising the temperature ($[\alpha]^{47}_{gr.} + 0{\cdot}2°$; the specific rotation is slightly higher in N-potassium chloride ($[\alpha]^{20}_{gr.} + 0{\cdot}4°$, $p = 11$), but this result is due to the fact that the potassium salt of benzoyl-*d*-alanine is much more dextrorotatory than the free acid in aqueous solution. It thus appears that the effect of neutral salts on the rotatory powers of amino-acids is due to the presence of the amino-group in these compounds.

Now the elevation of the rotation of ethyl *l*-aspartate by dissolution in hydrochloric acid or water is probably due to the nitrogen atom becoming quinquevalent ($\cdot NH_3Cl$, $\cdot NH_3\cdot OH$), and in the latter case there would probably exist in solution a mixture of the hydrated and non-hydrated forms of the amine. The rotatory values for the amino-acid and ester indicate similar constitutions in solution for both compounds, and it would thus appear that *l*-aspartic acid in aqueous solution consists mainly of the forms $CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$ and $CO_2H\cdot CH_2\cdot CH(NH_3\cdot OH)\cdot CO_2H$, the former being lævorotatory and the latter dextrorotatory. The relative amount of the hydrated form would diminish with rise of temperature. Further work on the rotatory powers of amino-

acids and their esters would be of interest in this connexion. The presence of neutral salts influences not only the rotatory powers, but the solubilities of amino-acids and proteins in aqueous solution. Schiff (*Ber.*, 1884, **17**, 2929) observed that aspartic acid dissolves more readily in aqueous ammonium chloride than in water, and suggested that this was due to the amino-acid exercising its basic and acidic functions, the compounds yielding an equilibrium mixture of ammonium aspartate, aspartic acid hydrochloride, and unchanged ammonium chloride. Sakurai (P., 1894, **10**, 90) ascribed the formula $CH_2(NH_3{\cdot}NO_3){\cdot}CO_2K$ to a compound of glycine with potassium nitrate described by Boussingault (*Annalen*, 1841, **39**, 310). Although unable to isolate this compound, Pfeiffer and von Modelski succeeded in preparing a large number of compounds of amino-acids with the haloids of the alkali and alkaline earth metals, and also regarded these compounds as "amphi" salts possessing the formulæ $Me'O{\cdot}CO{\cdot}R{\cdot}NH_3X$ or

$$Me''\!<\!\begin{matrix}O{\cdot}CO{\cdot}R{\cdot}NH_3X\\ O{\cdot}CO{\cdot}R{\cdot}NH_3X\end{matrix}$$

(*Zeitsch. physiol. Chem.*, 1912, **81**, 329; 1913, **85**, 1). This view was modified by Pfeiffer and Wittka, who regard the compounds of inorganic salts with amino-acids, carboxylic acids, esters, etc., as "molecular" compounds, without excluding the possibility that the halogen atom of the inorganic salt is combined with the amino-group of an amino-acid in the form of an ammonium salt (*Ber.*, 1915, **48**, 1289). Pfeiffer has also brought forward strong evidence that the compounds of amino-acids with neutral salts are capable of existence in aqueous solution (*Ber.*, 1915, **48**, 1938). Inasmuch as the amino-acids are amphoteric electrolytes possessing very small acid and basic constants (for alanine $K_a = 1{\cdot}9 \times 10^{-10}$, $K_b = 5{\cdot}1 \times 10^{-12}$), it does not seem possible for the halogen of the salts to be combined in the "ammonium" salt form, nor for compounds of the "amphi" salt type to exist to an appreciable extent in aqueous solution. Such an objection cannot be raised if the compounds are regarded as "molecular" compounds with the metallic atom co-ordinated with the oxygen of the carboxyl group or with the nitrogen of the amino-group (Pfeiffer, *loc. cit.*). The observed regularities in the effects of barium, calcium, and sodium haloids make it appear probable that the influence of salts on the rotatory powers of hydroxy- and amino-compounds is due to the same cause. It may therefore be assumed that this influence is due to combination of the salts with the optically active compounds in question, the latter reacting with the salts in consequence of the residual affinity of the oxygen and nitrogen atoms in the alkylic

hydroxyl and amidogen radicles respectively. It is thus no longer necessary to explain the alterations in rotatory power caused by the presence of neutral salts by means of the recently revived hypothesis of Arndtsen that the changes in rotatory power are due to a displacement in the equilibrium of hypothetical isodynamic forms of the active compound.

An examination of table X shows that there are certain regularities in the rotatory powers of the derivatives from the optically active α-amino-acids. The rotatory powers of the hydrochlorides of those varieties of the active amino-acids in this table are in every case more positive than those of the amino-acids in aqueous solution, and in general the molecular rotations of the potassium salts of the benzoylamino-acids are more positive than those of the hydrochlorides of the amino-acids. The aminoacylglycines possess relatively high positive rotations in aqueous solution, whilst the glycyl derivatives of the amino-acids in question are usually lævorotatory, glycyl-*l*-phenylalanine being a noticeable exception. Similar regularities are observable in the recorded values for the diketopiperazines, β-naphthalenesulphonyl, and *N*-methyl derivatives of the same amino-acids.

Fischer and Raske (*Ber.*, 1907, **40**, 3717) have transformed *l*-serine into *l*-β-chloro-α-aminopropionic acid, and the latter into *d*-alanine, without displacing groups directly attached to the asymmetric carbon atom, and they have pointed out that the hydrochlorides of these amino-acids possess more positive rotatory powers than the configuratively related parent acids. A similar regularity is evident in the rotatory powers of the related compounds *l*-asparagine and *l*-aspartic acid, and the author maintains that *the rotatory values for the amino-acids and their derivatives in table X indicate that all these compounds possess the same relative configurations.* The influence of temperature on the rotatory powers of *l*-asparagine, *l*-aspartic acid (T., 1915, **107**, 1509), and *d*-glutamic acid is similar to that on *d*-alanine in aqueous solution, and the rotatory powers of these compounds are increased by the addition of sodium or barium haloids. The similarity between *l*-aspartic acid and *d*-glutamic acid is shown admirably by the curves of Andrlík (*Zeitsch. Ver. deut. Zuckerind.*, 1903, 948) and Wood (T., 1914, **105**, 1988) illustrating the effect of varying amounts of bases on the rotations of these acids. It should also be pointed out that those amino-acids which have been obtained from protein occur in the optically active varieties denoted in table X. Moreover, Ehrlich observed that when certain inactive amino-acids were subjected to the action of yeast in sugar solutions, the forms which survived attack were the enantiomorphs of the naturally occurring

TABLE X.

The Optical Rotatory Powers ($[\alpha]_D^{20}$) *of α-Amino-acids and of certain Derivatives from them.*

Amino-acid.	Water.	Hydrochloric acid.	Benzoylamino-acid (in KOH,aq.).	Aminoacylglycine (in water).	Glycylamino-acid (in water).	Hydantoin.*
d-Alanine[1]	+ 2·7°	+ 14·3°	+ 36·5°	+ 50·2°	− 50·0°	+ 50·6° (water)
l-Serine[2]	− 6·8	+ 14·4	+ 43·6 (in NaOH,aq.) (*p*-nitrobenzoyl)	—	—	—
l-β-Chloro-α-aminopropionic acid[3]	− 15·5	+ 0·9	—	—	—	—
d-α-Aminobutyric acid[4]	+ 8·0	+ 19·6	+ 30·7 (in NaOH,aq.)	+ 86·4 (K) + 26·8 (A & C)	− 20·3	—
d-Valine[5]	+ 6·4	+ 28·7	—	+ 90	− 19·7	− 97·5 (phenylhydantoin in alcohol).
d-α-Aminohexoic acid[6]	—	+ 23·0	+ 21·9	—	—	—
l-Leucine[7]	− 10·3	+ 15·6	+ 6·6 (in NaOH,aq.)	+ 85·5	− 35·0	− 68·2 (in NaOH,aq.)

* Hydantoins, Dakin & Dudley, *J. Biol. Chem.*, 1913, **17**, 29; 1914, **18**, 48; T., 1915, **107**, 434.

[1] Fischer, *Ber.*, 1905, **38**, 2914; 1906, **39**, 453; 1907, **40**, 943.

[2] Fischer and Jacobs, *Ber.*, 1906, **39**, 2942; Fischer and Raske, *Ber.*, 1907, **40**, 3717.

[3] Fischer and Raske, *loc. cit.*

[4] Fischer and Mouneyrat, *Ber.*, 1900, **33**, 2383; Koelker, *Zeitsch. physiol. Chem.*, 1911, **73**, 312; Abderhalden and Chang, *ibid.*, 1912, **77**, 471.

[5] Fischer, *Ber.*, 1906, **29**, 2320; Fischer and Scheibler, *Annalen*, 1908, **363**, 136.

[6] Fischer and Hagenbach, *Ber.*, 1901, **34**, 3764.

[7] Fischer, *Ber.*, 1900, **33**, 2370; *Ber.*, 1906, **39**, 2893; Fischer and Steingroever, *Annalen*, 1909, **365**, 167.

TABLE X.—(*continued*).

The Optical Rotatory Powers ($[\alpha]_D^{20}$) *of* α-*Amino-acids and of certain Derivatives from them.*

Amino-acid.	Water.	Hydro-chloric acid.	Benzoylamino-acid (in KOH,aq.).	Aminoacylglycine (in water).	Glycylamino-acid (in water).	Hydantoin.*
d-*iso*Leucine[8]	+ 11·3°	+ 40·6°	+ 26·4° (in NaOH,aq.)	+ 33·6°	− 14·7°	—
l-Asparagine[9]	− 4·9	+ 28·5	—	—	− 6·4	—
l-Aspartic acid[10]	+ 4·3	+ 25·7	+ 37·4	—	+ 11·1	− 125 (in NaOH,aq.).
d-Glutamic acid[11]	+ 9·9	+ 30·8	+ 18·7	—	− 6·3	− 79 (in NaOH,aq)
l-Phenylalanine[12]	− 35·3	− 7·1	+ 17·1	+ 54·2	+ 41·4	− 96·4 (in 50 per cent. alcohol).
l-Tyrosine[13]	—	− 8·6	+ 19·2	—	—	− 143 (in NaOH,aq.)

* Hydantoins, Dakin and Dudley, *J. Biol. Chem.*, 1913, **17**, 29; 1914, **18**, 48; T., 1915, **107**, 434.

8 Locquin, *Bull. Soc. chim.*, 1907 [iv], **1**, 595; Abderhalden, Hirsch, and Schuler, *Ber.*, 1909, **42**, 3394.

9 Fischer and Koenigs, *Ber.*, 1904, **37**, 4585.

10 Fischer, *Ber.*, 1899, **32**, 2451; Fischer and Fiedler, *Annalen*, 1910, **375**, 181.

11 Fischer, Kropp, and Stahlschmidt, *Annalen*, 1909, **365**, 189.

12 Fischer and Mouneyrat, *loc. cit.*; Fischer and Schoeller, *Annalen*, 1907, **357**, 1.

13 Fischer, *Ber.*, 1899, **32**, 3638.

forms. The configurations of the constituent amino-acids also appear to condition the hydrolysis of polypeptides by enzymes; thus only those compounds containing the naturally occurring optically active forms of the amino-acids are hydrolysed by trypsin (Fischer and Abderhalden, *Zeitsch. physiol. Chem.*, 1907, **51**, 264). The optically active amino-acids appearing in table X may therefore be conveniently termed the "*l*"-aliphatic *α*-amino-acids.

It may be recalled that *l*-phenylaminoacetic acid was obtained by Ehrlich by the action of yeast on the optically inactive amino-acid. The rotatory values for this acid recorded by Fischer and Weichhold (*Ber.*, 1908, **41**, 1293) are $[\alpha]_D^{20}$ $-112{\cdot}6°$ (water), $-158°$ (*N*-hydrochloric acid), and $-260°$ for the formyl derivative, values which may be compared with those for *l*-phenylalanine, $[\alpha]_D^{20}$ $-35{\cdot}3°$ (water), $-7{\cdot}1°$ (hydrochloric acid), and $+75{\cdot}2°$ for the formyl compound. These results appear to show that *d*-phenylaminoacetic acid is related configuratively to the active amino-acids in table X.

The α-Halogen Acids.

The optically active halogen acids may be obtained from the active hydroxy-acids by phosphorus haloids or thionyl chloride, from the active amino-acids by nitrosyl chloride (or bromide), or by the resolution of the inactive compounds. The racemisation which usually accompanies reactions involving the displacement of groups attached to the asymmetric carbon atom and the reactivity of the halogen towards bases, frequently make it difficult to obtain the active forms of the halogen acids in a state of purity. There are necessarily fewer derivatives of the halogen acids than of the hydroxy- or amino-acids, and there is no doubt that some of the values given in the literature for halogen acids and derivatives from them are numerically lower than those for the pure active compounds. The values in table XI for certain *d*-*α*-halogen acids indicate the great probability that all these compounds possess the same configurations. Inasmuch as these optically active halogen acids are all dextrorotatory, their usual designation *d*- may also be used to indicate their configurative similarity to one another (see footnote, p. 547).

The rotatory powers of the esters of the *d*-*α*-halogen-propionic and -succinic acids diminish with increase of molecular weight, and it appears from the table that the glycines possess higher molecular rotatory powers than the parent acids. The specific rotatory power of *d*-bromopropionic acid diminishes with rise of temperature (Ramberg), as is also the case for methyl and ethyl *d*-*α*-chloropropionates (J. W. Walker) and for methyl *d*-bromosuccinate

TABLE XI.

The Specific Rotations ($[\alpha]_D^{20}$) *of certain* d-*α-Halogen Acids and their Derivatives.*

	Acid.	Methyl ester.	Ethyl ester.	Propyl ester	Bromoacyl-glycine.	References.
d-α-Chloropropionic acid	+ 14°*	+26·8° (at 5°)	+19·9 (at 5°)	+11·0° (at 6°)	—	Frankland and Garner, T., 1914, **105**, 1101; J. W. Walker, T., 1895, **67**, 918.
d-α-Bromopropionic acid	+ 29·0	+42·6	+35·5	+22	+35·3 (water)	J. W. Walker, *loc. cit.*, Ramberg, *Annalen*, 1909, **370**, 234; Fischer, *Ber.*, 1907, **40**, 489.
d-α-Bromo*iso*valeric acid	+ 9·0 (water); 22·8 (benzene)	—	—	—	+47·5 (alcohol)	Fischer and Scheibler, *Ber.*, 1908, **41**, 889, 2891.
d-α-Bromo*iso*hexoic acid	+ 49·4	—	+50	—	+62 (alcohol)	Fischer and Carl, *Ber.*, 1906, **39**, 3998.
d-α-Bromo-β-methylvaleric acid	+ 26·5 (benzene)	—	—	—	+64·4 (alcohol)	Abderhalden, Hirsch, and Schuler, *Ber.*, 1909, **42**, 3394.
d-α-Bromo-β-phenylpropionic acid	+ 10·4	—	+9	—	+14·6 (alcohol)	Senter, Drew, and Martin, this vol., p. 158; Fischer and Carl, *loc. cit.*; Fischer and Schoeller, *Annalen*, 1907, **357**, 1
d-Chlorosuccinic acid	+ 21·7 (water); 55·7 (ethyl acetate)	+42·3	+32·7	+25	—	Walden, *Ber.*, 1896, **29**, 1689; McKenzie and Barrow, T., 1911, **99**, 1919.
d-Bromosuccinic acid	+ 41·8 (water); 76·5 (ethyl acetate)	+51·2	+41·0	+38·0	—	Walden, *Ber.*, 1895, **28**, 1290, *Zeitsch. physikal. chem.*, 1895, **17**, 264.
d-Dichlorosuccinic acid............	+ 80·4 (ethyl acetate)	—	+66 (chloroform)	—	—	Holmberg, *Svensk. Kem. Tid.*, 1912; Darzens and Séjourné, *Compt. rend.*, 1912, **154**, 1615.
d-Dibromosuccinic acid	+ 70 (water)*; 148 (ethyl acetate)	—	—	—	—	Holmberg, *Svensk. Kem. Tid.*, 1911; McKenzie, T., 1912, **101**, 1196.

* Approximate values by calculation.

(Walden). On the other hand, Senter, Drew, and Martin find that the lævorotatory power of *l*-α-bromo-β-phenylpropionic acid is increased by rise of temperature.

It has been shown by Frankland and Turnbull (*loc. cit.*) that the optically active methyl αβ-dichloropropionate obtained by the action of phosphorus pentachloride on methyl *d*-glycerate is dextrorotatory, whereas the higher esters are lævorotatory. It would thus seem that these esters are related to the *d*-halogen acids in table XI, the temperature coefficients of the esters in question being similar in character to that of *d*-α-bromo-β-phenylpropionic acid. The rotations of the *d*-phenylhalogenacetic acids are considerably higher in benzene solution than in aqueous solution, and the specific rotation of the ethyl ester appears to be lower than that of the free acid (McKenzie and Barrow, T., 1911, **99**, 1919); moreover, the rotatory powers of the methyl and ethyl esters diminish with rise of temperature (J. W. Walker). These facts indicate that the dextrorotatory acids are configuratively related to *d*-chloropropionic acid.

The Relationship between the Optically Active α-Halogen Acids and α-Amino-acids.

The foregoing considerations render it possible to determine whether the conversions of the optically active α-amino-acids into the halogen acids which have been effected by nitrosyl haloids are or are not similar in stereochemical character. It has often been assumed that the action of nitrosyl haloids on the active amino-acids is always of the same character, but it is certain that a given reagent does not invariably act in the same way on compounds of similar type. The following conclusions may be drawn from the relationships which have been established for the active α-amino-acids and α-bromo-acids respectively:

(*a*) The transformations *d*-alanine ⟶ *l*-bromopropionic acid, *l*-aspartic acid ⟶ *l*-chlorosuccinic acid (or *l*-bromosuccinic acid), *d*-valine ⟶ *l*-α-bromo*iso*valeric acid, *l*-leucine ⟶ *l*-α-bromo*iso*hexoic acid, *d*-*iso*leucine ⟶ *l*-α-bromo-β-methylvaleric acid, and *l*-phenylalanine ⟶ *l*-α-bromo-β-phenylpropionic acid (by the action of nitrosyl haloids), are all of the same stereochemical character, that is to say, they are either all "normal" or all "abnormal" reactions. Inasmuch as *d*-glutamic acid and *d*-α-aminobutyric acid are, according to the author, related to the above amino-acids, it is almost certain that the changes *d*-glutamic acid ⟶ *l*-α-chloroglutaric acid ($[\alpha]_D^{25}$ $-12{\cdot}5°$ in water) and *l*-α-aminobutyric acid ⟶ *d*-α-bromobutyric acid ($[\alpha]_D$ $+15{\cdot}4°$, Abderhalden and Chang, *loc.*

cit.) are also of this type (for references, see Frankland, T., 1913, **103**, 728).

(*b*) The action of nitrosyl bromide on esters of *d*-alanine, *l*-aspartic acid, *l*-leucine, and *l*-phenylalanine is opposite in character to that of this reagent on the amino-acids mentioned in paragraph (*a*).

(*c*) The action of ammonia on *l*-α-bromopropionic acid (or ester), *l*-bromosuccinic acid, *l*-α-bromo*iso*valeric ester, *l*-α-bromo*iso*hexoic acid (or ester), *l*-α-bromobutyric acid or *l*-α-bromo-β-phenylpropionic acid is opposite to that of nitrosyl bromide on the amino-acids mentioned in paragraph (*a*). Fischer has shown that the action of potassium phthalimide on ethyl *l*-α-bromopropionate (*Ber.*, 1907, **40**, 489), that of trimethylamine on *d*-α-bromopropionic acid (*Ber.*, 1907, **40**, 5000), and that of methylamine on *l*-α-bromopropionic acid, *d*-α-bromo*iso*hexoic acid, or *d*-α-bromo-β-phenylpropionic acid, all take place in the same stereochemical sense as the action of ammonia on the same compounds (Fischer and von Mechel, *Ber.*, 1916, **49**, 1355). It is exceedingly probable that the numerous examples of the action of ammonia on the active α-bromoacyl derivatives of amino-acids which have been investigated by Fischer and Abderhalden are all of this type.

(*d*) The action of ammonia on *l*-α-bromo*iso*valeric acid or on *l*-α-bromo-β-methylvaleric acid is the reverse of that of the same reagent in the examples given in paragraph (*c*).

In order to decide in which of the above reactions a change of configuration takes place, it becomes necessary to ascertain whether the active α-amino-acids in table X possess the same relative configurations as the *d*-halogen acids in table XI. Although these two classes of compounds can scarcely be considered to be "similarly constituted," it is desirable that a comparison of the rotatory powers of their derivatives should be made in this connexion. Unfortunately, there are very few similar classes of derivatives of the amino-acids on the one hand and of the halogen acids on the other the rotatory powers of which are available for a comparative study of these compounds. The most complete series of derivatives are the α-bromoacyl- and the α-aminoacyl-amino-acids. It is evident from table XII that there is a close relationship between the values for the aminoacyl derivatives and the bromoacyl derivatives from which they are obtained, and it appears to the author that this relationship indicates the great probability that the amino-derivatives are configuratively related to the bromo-derivatives in question. For example, *d*-α-bromopropionyl-*l*-alanine ($[\alpha]_D$ $+68{\cdot}2$) is related to *d*-alanyl-*l*-alanine ($[\alpha]_D$ $+68{\cdot}9$), and not to *l*-alanyl-*l*-alanine ($[\alpha]_D$ $+21{\cdot}6$). If, for the purpose of this

TABLE XII.

The Optical Rotatory Powers ($[\alpha]_D^{20}$) *of certain α-Bromoacyl and α-Aminoacyl Derivatives of the α-Amino-acids.*

Amino-acid.	Amino-acid.	Chloroacetyl-amino-acid.	Glycyl-amino-acid.	*d*-α-Bromo-propionyl-amino-acid.	*d*-Alanyl-amino-acid.	*d*-α-Bromo-*iso*hexoylamino-acid.	*l*-Leucylamino-acid	References.
Glycine	—	—	—	+ 38·3°	+ 50·2°	+ 62·0° (in alcohol)	+ 86·0°	Fischer, *Ber.*, 1908, **41**, 850; 1906, **39**, 2911.
d-Alanine	+ 2·7°	− 45°	− 50°	− 16·5	− 21·6	+ 23·3 (in alcohol)	+ 23·5 (in methyl alcohol)	Fischer, *Ber.*, 1906, **39**, 453; Fischer and Schulze, *Ber.*, 1907, **40**, 943.
l-Alanine	− 2·7	+ 45	+ 50	+ 68·2	+ 68·9	—	—	Fischer and Raske, *Ber.*, 1906, **39**, 3989.
l-Leucine	− 10·3	− 13·8	− 35·2	+ 2·0 (in alcohol)	− 17·0	+ 16·2 (in ethyl acetate)	− 13·4 (in *N*-NaOH)	Fischer, *Ber.*, 1907, **40**, 1754.
d-Leucine	+ 10·3	+ 13·8	+ 35·2	—	—	+ 35 (in ethyl acetate)	+ 68·9 (in *N*-HCl)	Fischer and Koelker, *Annalen*, 1907, **354**, 39.
d-*iso*Leucine ...	+ 10·5	+ 25·0 (in alcohol)	− 14·7	+ 24·5 (in alcohol)	+ 6·1 (in HCl)	+ 49 (in ethyl acetate)	+ 18·1	Abderhalden, Hirsch, and Schuler, *Ber.*, 1909, **42**, 3394.
l-*iso*Leucine ...	− 10·5	− 25·0 (in alcohol)	+ 14·7	—	—	+ 19 (in alcohol)	+ 53·1	Abderhalden and Schuler, *Ber.*, 1910, **43**, 907.

The values in this table are for the specific rotations in aqueous solution unless stated otherwise.

discussion, the active amino-acids in table X be denoted by the designation "*l*," it follows that the "*l*" amino-acids possess the same configuration as the *d*-halogen acids,* and that the action of ammonia on the above halogen acids (with the exception of α-bromo*iso*valeric acid and α-bromo-β-methylvaleric acid) or their derivatives does not cause a configurative change. It may be mentioned in this connexion that Scheibler has conclusively shown that the action of ammonia on *l*-ββ′-iminodibutyric acid, yielding *l*-β-aminobutyric acid, is a "normal" action (*Ber.*, 1912, **45**, 2272). The transformations of the aliphatic α-amino-acids (including phenylalanine), with the exception of valine and *iso*leucine, may be represented by the following scheme (compare Frankland, T., 1913, **103**, 741):

	d-α-Halogen acid	⟷	*d*-α-halogen ester (or glycine)
	↓ NH_3		NOBr ↑↓ NH_3
	"*l*"-α-amino-acid	⟷	"*l*"-α-amino-ester (or glycine)
NOBr	↓ NOBr		
	l-α-halogen acid	⟷	*l*-α-halogen ester (or glycine)
	↓ NH_3		NOBr ↑↓ NH_3
	"*d*"-α-amino-acid	⟷	"*d*"-α-amino-ester (or glycine)

The scheme for "*l*"-valine and "*l*"-*iso*leucine is similar, except that the action of ammonia on the free bromo-acids is assumed to be "abnormal." *iso*Leucine contains two asymmetric carbon atoms, and a true Walden inversion cannot be effected, but the transformations involved are similar to those for valine.

The Relationship between the Optically Active α-Amino- and α-Hydroxy-acids.

It is clear from the relationships which have been established for the amino-acids and hydroxy-acids, respectively, that the trans-

* It appears advisable to retain for the present the designation *d*- for the dextrorotatory α-halogen acids to denote their configurative similarity to one another. If the above view that these dextrorotatory α-halogen acids are related configuratively to the "*l*"-α-amino-acids is correct, it would be preferable to indicate their configurations by the prefix "*l*-." It may be mentioned here that it is not possible to denote the relative configuration of a given optically active compound (containing only one asymmetric carbon atom) always by means of the same prefix (Clough, P., 1913, **29**, 359).

formations (effected by nitrous acid) *d*-alanine → *d*-lactic acid, *l*-serine → *d*-glyceric acid, *d*-valine → *d*-α-hydroxy*iso*valeric acid, *l*-leucine → *l*-α-hydroxy*iso*hexoic acid, *l*-aspartic acid → *l*-malic acid, *d*-glutamic acid → *l*-α-hydroxyglutaric acid, and *l*-phenylalanine → *l*-β-phenyl-lactic acid (Clough, unpublished) are all of the same stereochemical type. It is not possible with the data at present available to make a satisfactory comparison of the rotatory powers of the active hydroxy-acids with those of the active amino-acids. The rotatory powers of very few α-amino-esters have been determined, and of only two hydroxyacylglycines. There are, however, certain similarities which seem to indicate that the "*l*"-α-amino-acids possess the same relative configurations as the "*l*"-hydroxy-acids (which are enantiomorphously related to *d*-tartaric acid).

The dextrorotatory powers of "*l*"-lactic acid and "*l*"-glyceric acid in aqueous solution are reversed and the lævorotatory power of *l*-malic acid is increased on raising the temperature; the dextrorotatory powers of "*l*"-alanine and *l*-aspartic acid are reversed and that of "*l*"-glutamic acid is diminished with rise of temperature. Moreover, the changes in the rotatory powers of "*l*"-alanine, *l*-asparagine, *l*-aspartic acid (or ester), "*l*"-glutamic acid, "*l*"-lactic acid (or ester), and *l*-malic acid (or ester) caused by inorganic haloids in aqueous solution are all in the same sense. It is therefore suggested that the action of nitrous acid on the active aliphatic α-amino-acids is a "normal" action.

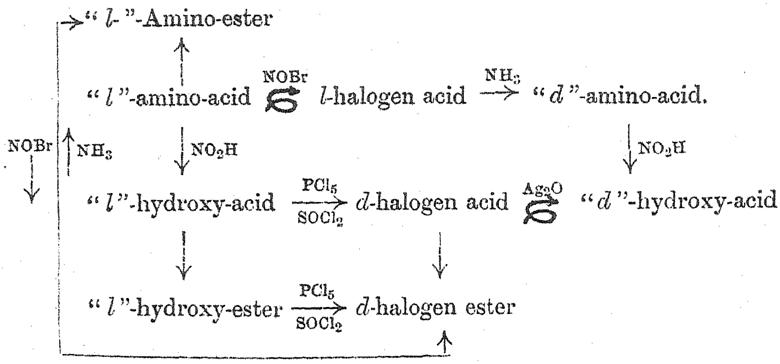
The Relationship between the Optically Active α-Hydroxy- and α-Halogen Acids.

The conclusions that have been drawn regarding the configurative relationships of the hydroxy-acids on the one hand and of the halogen acids on the other make it appear almost certain that the conversions of "*l*"-lactic acid (or ester) by phosphorus haloids or thionyl chloride into *d*-halogen-propionic acids (or esters), *l*-malic acid (or esters) by phosphorus pentachloride or thionyl chloride into *d*-chlorosuccinic acid (or esters), ethyl *l*-α-hydroxy*iso*hexoate by phosphorus and bromine into ethyl *d*-α-bromo*iso*hexoate, and of ethyl *d*-tartrate by thionyl chloride into ethyl *l*-dichlorosuccinate, are reactions of the same stereochemical character. When it is remembered that the specific rotatory powers of the *d*-halogen esters diminish as the homologous series are ascended, and that the rotatory powers of the *d*-bromo-esters are more positive than those of the corresponding chloro-esters, it

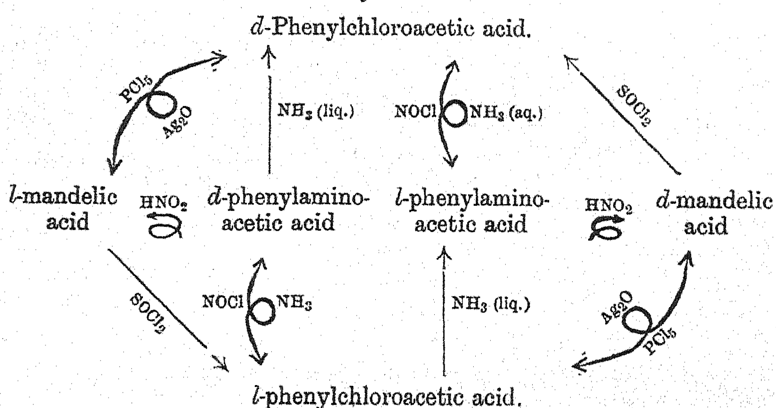
is not surprising that the lævorotatory esters of "*l*"-glyceric acid yield, on treatment with phosphorus pentachloride, esters of $\alpha\beta$-dichloropropionic acid diminishing in rotatory power from a positive value for the methyl ester to negative values for the higher esters, and that *iso*butyl *l*-α-hydroxybutyrate yields a lævorotatory chloro-ester but a dextrorotatory bromo-ester, these halogen esters being derived, presumably, from α-chloro- and α-bromo-butyric acids possessing the same configurations as *d*-chloropropionic acid (Guye and Jordan, *Bull. Soc. chim.*, 1896, [iii], **15**, 495). It appears probable that the relationship between the optically active aliphatic normal secondary alcohols and the halogen compounds prepared from them by hydrogen haloids, and that between *l*-β-hydroxybutyric acid (or ester) and *d*-β-chlorobutyric acid (or ester) obtained from it by phosphorus pentachloride, are also of the same character. There is little doubt that thionyl chloride would react with these hydroxy-compounds in the same manner as hydrogen haloids or phosphorus pentachloride respectively.

If it is assumed that the "*l*"-amino-acids are related to the *d*-halogen acids and also to the "*l*"-hydroxy-acids, it follows that the "*l*"-hydroxy-acids are of the same configuration as the *d*-halogen acids. It may be recalled that the temperature–rotation curves for ethyl *d*-bromopropionate and ethyl *d*-bromosuccinate are similar in character to those of *d*-("*l*-")lactic acid (or ester) and *l*-malic acid (or ester). On the other hand, the influence of temperature on methyl *d*-$\alpha\beta$-dichloropropionate is opposite to that on methyl "*l*"-glycerate, from which it is prepared.

The fact that the rotatory powers of the *d*-halogen esters diminish as the carbalkyloxy-groups increase, whilst the rotations of the *d*-hydroxy-esters increase as the series is ascended (at least for the early members), is in accordance with the above view. It may therefore be assumed that the action of phosphorus haloids and of thionyl chloride on the aliphatic α-hydroxy-acids (or esters) which have been investigated is not accompanied by a change of configuration. The following scheme would then include most of the changes which have so far been realised with α-derivatives of propionic acid, butyric acid, succinic acid, *iso*hexoic acid, and (with the possible exception of the action of thionyl chloride) β-phenylpropionic acid:



It has been suggested above that *l*-mandelic acid is configuratively allied to *d*-malic acid, that the *l*-phenyl-halogen-acetic acids are related to *l*-chlorosuccinic acid, and that *l*-phenylaminoacetic acid has a similar configuration to that of *d*-aspartic acid. Inasmuch as it has been assumed that *l*-chlorosuccinic acid is configuratively related to *d*-malic acid and to *d*-aspartic acid, it would follow that *l*-mandelic acid, the *l*-phenyl-halogen-acetic acids, and *l*-phenylaminoacetic acid all possess the same relative configurations. In any case, it is almost certain from the rotatory powers of the latter compounds that their common designation (*l*-) may also be used to imply a similar configurative relationship. The following scheme, then, represents most of the transformations of the derivatives of phenylacetic acid, and also (as far as they have been studied) those of the β-derivatives of β-phenylpropionic acid and of the α-derivatives of α-phenylpropionic acid, with the exception of those reactions of the latter in which complete racemisation occurs. The reactions which have been effected with esters of the acids are likewise in conformity with this scheme.



Summary of Conclusions.

(*a*) A comparison of the optical rotatory powers of the acids commonly written *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid (which possess the same relative configurations), and of derivatives from them, has led the author to assume that *the optical rotatory powers of similarly constituted compounds possessing the same configuration are, in general, influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom.*

(*b*) The rotatory powers of the above four acids, and also of *d*-α-hydroxybutyric acid, *l*-α-hydroxy*iso*valeric acid, *d*-α-hydroxy*iso*-hexoic acid, *d*-α-hydroxy-β-phenylpropionic acid, *d*-α-hydroxy-glutaric acid and their derivatives, indicate that all these acids possess the same relative configurations. For the sake of convenience, the designation "*d*" has been used to denote the configurations of these compounds.

(*c*) Similarly, it is assumed that the naturally occurring α-amino-acids, commonly denoted as *d*-alanine, *l*-serine, *l*-aspartic acid, *d*-valine, *l*-leucine, *d*-*iso*leucine, *d*-α-aminobutyric acid, *d*-glutamic acid, *l*-phenylalanine, and *l*-tyrosine, all possess the same configurations. The configurations of these compounds have been denoted by the symbol "*l*."

(*d*) The dextrorotatory (*d*-) α-halogen acids which have been isolated are assumed to be configuratively similar compounds.

(*e*) A comparison of the rotatory powers of the optically active α-bromoacyl-amino-acids with those of the α-aminoacyl-amino-acids leads to the view that the amino-acids mentioned in paragraph (*c*) are related configuratively to the halogen acids mentioned in paragraph (*d*).

(*f*) It is suggested that the "*d*"-hydroxy-acids are enantiomorphously related to the "*l*"-amino-acids, and therefore to the *d*-halogen acids.

(*g*) The lævorotatory compounds, *l*-mandelic acid, *l*-phenylchloroacetic acid, and *l*-phenylaminoacetic acid, are assumed to possess the same configurations.

Experimental Data.

l-*Lactic Acid.*

The aqueous lactic acid was obtained by the hydrolysis of methyl *l*-lactate by boiling with ten times its weight of water for six

hours, and subsequent distillation of the methyl alcohol. This specimen contained 92 per cent. of *l*-lactic acid and 8 per cent. of *d*-lactic acid.

$p = 10{\cdot}73$.

t	15°.	18°.	36°.	52°.	62°.	70°.	15°.
d^t	1·03	1·03	1·02	1·01	1·01	1·00	1·03
$\alpha^t_{gr.}(l = 4)$	−0·95°	−0·88°	−0·32°	±0·00°	+0·18°	−0·30°	−0·95°
$[\alpha]^t_{gr.}$	−2·2°	−2·0°	−0·7°	±0·0°	+0·4°	+0·7°	−2·2°

A specimen of *l*-lactic acid prepared from zinc *l*-lactate showed similar behaviour.

Methyl l-*Lactate.*

This ester was prepared from zinc *l*-lactate, obtained from a dextrorotatory lactic acid syrup, which gave $\alpha_D(l=1)+5{\cdot}2$, by Patterson and Forsyth's method (T., 1913, **103**, 2263). The specimen contained about 5 per cent. of methyl *d*-lactate.

	d^t.	$\alpha^t_D(l = 1)$.	$\alpha^t_{gr.}$.	$\alpha^t_{vi.}$.	$[\alpha]^t_D$.	$[\alpha]^t_{gr.}$.	$[\alpha]^t_{vi.}$.*
15°	1·097	+7·96°	+9·05°	+11·95°	+7·26°	+8·25°	+10·89°
20	1·093	+8·15	9·17	12·25	7·46	8·39	11·21

* The rotations recorded in this paper and in the previous paper (*loc. cit.*) for mercury violet light ($[\alpha]_{vi.}$) are for $\lambda = 4078$.

Methyl l-*Lactate in Water.*

p.	d^{20}.	$\alpha^{20}_D(l = 1)$.	$\alpha^{20}_{gr.}$.	$\alpha^{20}_{vi.}$.	$[\alpha]^{20}_D$.	$[\alpha]^{20}_{gr.}$.	$[\alpha]^{20}_{vi.}$
100	1·093	+8·15°	+9·17°	+12·25°	+7·46°	+8·39°	+11·21°
80·0	1·086	3·60	3·81	3·90	4·1	4·4	4·5
50·9	1·063	1·16	1·34	0·54	2·1	2·5	1·0
20·0	1·026	0·72 ($l = 2$)	0·73	−0·08	1·8	1·8	−0·2
10·0	1·012	0·27 ($l = 2$)	0·29	−0·10	1·3	1·4	−0·5
5·36	1·005	0·28 ($l = 4$)	0·30	−0·30	1·3	1·4	−0·9

d-*Alanine in Water.*

The specimen employed was prepared from silk by Fischer's method (*Ber.*, 1906, **39**, 462).

$p = 5{\cdot}85$.

t	13°.	16°.	29°.	40°.	64°.	74°.	80°.
d	1·02	1·02	1·01	1·01	1·00	1·00	1·00
$\alpha^t_{gr.}(l = 4)$	+0·74°	0·68°	0·56°	0·40°	0·04°	−0·04°	−0·15°
$[\alpha]^t_{gr}$	+3·1°	2·9°	2·4°	1·7°	0·2°	−0·2°	−0·6°

$p = 9{\cdot}81$.

t	15°.	20°.	30°.	45°.	60°.	72°.
d^t	1·03	1·03	1·03	1·02	1·02	1·01
$\alpha^t_{gr.}(l = 4)$	+1·41°	1·32°	1·10°	0·77°	0·48°	0·29°
$[\alpha]^t_{gr.}$	+3·5°	3·3°	2·7°	1·9°	1·2°	0·7°

d-Alanine in Aqueous Sodium Hydroxide (1 mol.).

$p=7\cdot79$, d^{15} 1·045, $\alpha^{15}_{gr.}$ $(l=2)$ $+1\cdot06°$, $[\alpha]^{15}_{gr.}$ $+6\cdot5°$.
$p=1\cdot61$, d^{15} 1·01, $\alpha^{15}_{gr.}$ $(l=4)$ $+0\cdot38°$, $[\alpha]^{15}_{gr.}$ $+5\cdot8°$.

d-Alanine in Hydrochloric Acid.

$p=8\cdot098$ (1 mol. HCl); d^{15} 1·036, α^{15}_{D} $(l=2)+2\cdot40°$, $\alpha^{15}_{gr.}$ $+2\cdot88°$, $[\alpha]^{15}_{D}+14\cdot3°$, $[\alpha]^{15}_{gr.}+17\cdot1°$.

$p=5\cdot605$ (1·5 mols. HCl); d^{15} 1·033, α^{l}_{D} $(l=2)+1\cdot70°$, $\alpha^{15}_{gr}+2\cdot06°$, $[\alpha]^{15}_{D}+14\cdot7°$, $[\alpha]^{15}_{gr.}$ $+17\cdot8°$.

Ethyl l-*Aspartate.*

This ester was prepared by Fischer's method (*Ber.*, 1901, **34**, 452).

d^{20} 1·085, α^{20}_{D} $(l=0\cdot5)$, $-5\cdot39°$, $\alpha^{20}_{ye.}$ $-5\cdot60°$, $\alpha^{20}_{gr.}$ $-6\cdot36°$, $\alpha^{20}_{vi.}$ $-13\cdot33°$, $[\alpha]^{20}_{D}$ $-9\cdot93°$, $[\alpha]^{20}_{ye.}$ $-10\cdot32°$, $[\alpha]^{20}_{gr.}$ $-11\cdot72°$, $[\alpha]^{20}_{vi.}$ $-24\cdot57°$.

d-*Glutamic Acid.*

Water; $p=0\cdot99$.

t	d^t.	$\alpha^t_D(l=4)$.	α^t_{gr}.	$[\alpha]^t_D$.	$[\alpha]^t_{gr.}$.
15°	1·004	+ 0·41°	+ 0·52°	+ 10·3°	+ 13·1°
40	0·995	0·32	0·43	8·1	10·9
51	0·992	0·29	0·40	7·4	10·2
60	0·998	0·27	0·37	6·9	9·5
*25**	—	—	—	*9·4*	*12·4*

* Interpolated.

$p=1\cdot50$.

25°	1·003	0·66	0·80	11·0	13·3

$p=2\cdot91$.

44°	1·002	1·20	1·44	10·3	12·3
64	0·994	1·00	1·25	8·6	10·8
75	0·990	0·90	1·15	7·8	10·0
25	—	—	—	*11·7*	*14·0*

Hydrochloric acid (N), 1·5 mols.; $p=8\cdot752$.

t.	d^t.	$\alpha^t_D(l=2)$.	$\alpha^t_{gr.}$.	$\alpha^t_{vi.}$.	$[\alpha]^t_D$.	$[\alpha]^t_{gr.}$.	$[\alpha]^t_{vi.}$.
13°	1·048	+ 5·81°	7·05°	15·60°	31·7°	38·4°	85·1°
32	1·042	5·50	6·72	14·65	30·2	36·8	80·3
43	1·037	5·32	6·53	14·10	29·3	36·0	77·7
25	—	—	—	—	*30·7*	*37·4*	*82·1*

Aqueous sodium hydroxide (1 mol.).

$p=21{\cdot}2$, $[\alpha]^{25}_{\text{gr.}}$ $-0{\cdot}8°$; $p=12{\cdot}25$, $[\alpha]^{25}_{\text{gr.}}$ $-3{\cdot}6°$; $p=2{\cdot}86$, $[\alpha]^{25}_{\text{gr.}}$ $-6{\cdot}1°$.

Aqueous sodium hydroxide (2 mols.).

$p=6{\cdot}56$, $[\alpha]^{25}_{\text{gr.}}$ $+11{\cdot}7°$; $p=1{\cdot}44$, $[\alpha]^{25}_{\text{gr.}}$ $+10{\cdot}2°$; $[\alpha]^{40}_{\text{gr.}}$ $+8{\cdot}6°$.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant towards the expense of this investigation, and to Dr. J. K. Wood for a supply of synthetic alanine from which the active benzoylalanine was prepared. The experimental portion of this work was performed at Birkbeck College, London.

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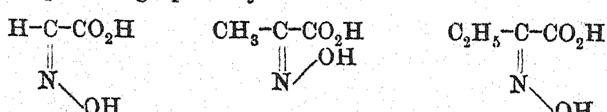
[*Received, March 25th, 1918.*]

XLV.—*The Dissociation Constants of some Higher Members of the α-Oximino-fatty Acids.*

By CEDRIC STANTON HICKS.

HANTZSCH and Miolati (*Zeitsch. physikal. Chem.*, 1892, **10**, 1), in an investigation of the dissociation constants of the lower members of the α-oximino-fatty acids, drew the conclusion that in the series $C_nH_{2n+1}{\cdot}C({:}NOH){\cdot}CO_2H$ as the series is ascended the dissociation constant diminishes in value, not steadily, but by a series of oscillations. Thus it was found that *K* for the first four acids, in which a hydrogen atom is successively displaced by the methyl, ethyl, and propyl groups, varied as follows: 0·0995, 0·0514, 0·0830, and 0·0685.

They considered that the variations were due to alternate fluctuations in the proximity of the hydroxyl to the carboxyl group, nearness of the hydroxyl, according to them, weakening the acid. This may be expressed graphically thus:



(I.) (II.) (III.)

As pointed out by Inglis and Knight (T., 1908, **93**, 1595), if the value for the second acid is abnormal, the series loses its interest,

and they accordingly began a reinvestigation of the conductivities of these acids.

In continuation of the work begun by these authors, an investigation of the dissociation constants of the higher members of the series has been undertaken.

EXPERIMENTAL.

The acids were prepared by Bouveault and Locquin's method (*Bull. Soc. chim.*, 1904, [iii], **31**, 1055) (compare Inglis and Knight, *loc. cit.*).

In the case of ethyl α-oximinohexoate, treatment with cold potassium hydroxide furnishes the potassium salt of the ester, the oximino-group thus acting as a negative group; when warmed with two molecular proportions of the alkali, the solution being acidified in the cold, the potassium salt (N·OK) separated, from which the acid was obtained on warming with hydrochloric acid.

Determination of Conductivities.

Owing to alterations in the laboratory being in progress at this time, it was impossible to prepare water with a smaller specific conductivity than $3{\cdot}3 \times 10^{-6}$.

The conductivity measurements were carried out at 25°, and owing in some cases to the rapid decomposition of the acids, together with the high conductivity of the water, measurements were not continued past a dilution of 256. All measurements except those at a dilution of 16 litres were duplicated. Since the conductivity was found to rise with the time, in order to obtain uniformity all measurements were made ten minutes after each successive dilution.

In the case of α-oximino-β-phenylpropionic acid, solution could only be effected by the aid of heat, even at a dilution of $N/32$. The solution, however, was evidently supersaturated, for after some hours crystals separated from it.

The values for Λ_∞ were calculated by means of Ostwald's empirical law, making use of the number of atoms in the molecule. The agreement between the values obtained in this way and those obtained from the sodium salt showed sufficient agreement in the case of the lower members to warrant the use of the same method for the higher members of the series (see Inglis and Knight, *loc. cit.*).

Equivalent Conductivities of the Acids.

α-Oximinoisovaleric Acid (m. p. 151·5°). $\Lambda_\infty = 378$.

$V =$	16	32	64	128	256
$\Lambda_v =$	48·15	66·5	87·5	110·8	136·8
$K =$	0·116	0·117	0·109	0·094	0·071

Mean value of K from the first three measurements = 0·114.

α-Oximino-n-hexoic Acid * (m. p. 131—132°. $\Lambda_\infty = 377$.

$V =$	32	64	128
$\Lambda_v =$	51·6	69·7	91·9
$K =$	0·0679	0·0656	0·0615

Mean K = 0·0650.

* The *ethyl* ester, $C_8H_{15}O_3N$, which has not been described, melts at 42°.

α-Oximinoisohexoic Acid (m. p. 150—151°). $\Lambda_\infty = 377$.

$V =$	16	32	64	128	256
$\Lambda_v =$	32·8	47·0	64·1	88·75	119·4
$K =$	0·0515	0·054	0·055	0·057	0·056

Mean K = 0·056.

α-Oximino-β-phenylpropionic Acid (m. p. 163°). $\Lambda_\infty = 377$.

$V =$	32	64	128	256
$\Lambda_v =$	49·5	67·7	89·7	118·7
$K =$	0·062	0·061	0·058	0·056

Mean K = 0·57.

α-Oximinophenylacetic Acid (m. p. 127°). $\Lambda_\infty = 379$.

Recalculated from Hantzsch and Miolati's results.

$V =$	16	32	64	128	256
$\Lambda_v =$	55·05	75·37	101·48	133·9	172·2
$K =$	0·1536	0·1545	0·1531	0·1508	0·1478

Mean K = 0·1519.

Stability of Acids in Aqueous Solution.

In order to obtain, if possible, some idea of the nature of the decomposition undergone by these acids in solution, an approximately $N/40$-solution of α-oximino*iso*valeric acid was placed in the thermostat at 25°. The strength of the acid was estimated at intervals by titration with $N/20$-sodium hydroxide.

The following are the values obtained, 5 c.c. of acid being employed for each titration:

Time in hours ...	0	2·5	3·5	5·5	21·5
Titre in c.c.	2·67	1·7	1·62	1·4	0·8

An attempt to determine the velocity constant for this decomposition was unsuccessful, owing probably to the doubtful nature of the products, of which carbon dioxide is one, but the concentration of which is uncertain. The result therefore only shows the diminution in strength approximately.

Discussion of Results.

Owing to the unstable nature of the higher members of this series of acids, little definite conclusion can be drawn.

The rise of conductivity with the time may mean a change from one isomeride into another, or it may simply mean a gradual decomposition, the conductivity ultimately becoming that of a complex solution.

It seems certain, however, that the oximinic hydroxyl group, rather than acting as an alcoholic group, as was implied by Hantzsch and Miolati, acts negatively, and so would lead to the greater strength of the "syn" acid, not the "anti" modification. There seems to be some anomalies in Hantzsch's conclusions as regards configuration, for (*Ber.*, 1891, **24**, 36) he states that the acetyl derivative of the α-oximinophenylacetic acid, melting at 145°, is decomposed by carbonate into the nitrile, carbon dioxide, etc., whilst that melting at 127° gives the original oxime. Since the melting point is a decomposition point, we should expect the "syn" acid to decompose more readily, that is, at the lower temperature. Again (*ibid.*), he states that the "syn" oxime is converted into the "anti" acetyl derivative by the process of acetylation, and since no mention of the preparation of the "syn" oxime is given, it is difficult to accept this as final.

Judging from the above results, and those obtained by Inglis and Knight, it seems, as was stated by these authors in connexion with the lower members, that the relation between configuration and dissociation constants is not so simple as was supposed, and an attempt to utilise the melting point as a means of assisting in the conclusion is just as unsatisfactory in its result.

One might expect to find some relation between the instability of the acids in aqueous solution and the configuration of their molecules; now in the case of α-oximino*iso*valeric acid, the strength diminished in twenty-one and a-half hours from $0{\cdot}031N$ to $0{\cdot}008N$, whilst in the case of α-oximino*iso*hexoic acid, the strength only fell from $0{\cdot}031N$ to $0{\cdot}026N$ in twenty-four hours.

Here we have no simple relation in the change of titre, because, applying Bischoff's dynamic theory, the obvious conclusion would be that α-oximino*iso*hexoic acid would be the less stable of the

two, since the two methyl groups in the 5-position with respect to the hydroxyl of the oximino-group ought to force the hydroxyl and carboxyl groups nearer together and cause instability; but this is inconsistent with the fact that α-oximino*iso*hexoic acid is one of the easiest to prepare, and it is also fairly stable in aqueous solution, the titre falling off only slightly in twenty-four hours.

On the other hand, α-oximino*iso*hexoic acid may have the "anti" configuration, and this would be consistent with the fact that α-oximino*iso*valeric acid is much stronger than α-oximino*iso*hexoic acid. α-Oximinophenylacetic acid has a higher dissociation constant than α-oximino-β-phenylpropionic acid. This may be partly due to space relationships and partly due to the negative character of the phenyl group.

According to Bischoff and Hedenström (*Ber.*, 1902, **35**, 4096), it seems that, in general, the phenyl esters are hydrolysed with greater difficulty than the benzyl esters, thus pointing to hindrance due to the closeness of the nucleus; this same closeness would lead to proximity of oximino- and carboxyl groups, and thus to a stronger acid. As regards purely aliphatic acids, however, all that can be said at the present juncture is that there is strong evidence of the oximino-group reacting negatively, but that general conclusions as regards the series are unjustifiable.

My thanks are due to Dr. J. K. H. Inglis, at whose suggestion these experiments were carried out, for his guidance and assistance during the investigation.

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[*Received May 13th*, 1918.]

The Principles of Diffusion, their Analogies and Applications.

A Lecture delivered before the Chemical Society on June 6th, 1918.

By Horace T. Brown, LL.D., F.R.S.

How it comes about that one who is neither physicist nor mathematician should have the temerity to address you on the subject I have chosen for my lecture requires a few words of explanation.

I was perforce led to the study of the phenomena of diffusion some twenty years or so ago when investigating the photosynthetic processes which go on in the green organs of plants. A serious difficulty occurred in finding an explanation of the mode by which the assimilatory centres of a leaf can be supplied with the highly dilute carbon dioxide of the air with sufficient rapidity to account for the observed rate of increase of carbohydrates in a leaf lamina placed under favourable conditions of insolation.

Some idea of the required magnitude of this gaseous flow may be gathered from the fact that when a leaf is actively assimilating, it may happen that its surface is taking in atmospheric carbon dioxide more than half as fast as an equal area of a concentrated solution of alkali hydroxide would do if submitted to a constantly renewed current of air with the same carbon dioxide content.

This would be a surprising fact even if we regarded the whole surface of the leaf as being permeable to atmospheric carbon dioxide, but we now know with certainty that the leaf cuticle is impervious to carbon dioxide at partial pressures considerably above those at which it occurs in the air, and that the whole of the gaseous exchanges incident to assimilation take place by free diffusion through the stomata, minute apertures in the cuticle which only represent from about 1 to 3 per cent. of the total surface area of the leaf. Hence it follows that these minute openings must have the power of drinking in atmospheric carbon dioxide at a rate about fifty times greater than apertures of similar dimensions would do if they were filled completely with a constantly renewed solution of alkali hydroxide.

This led me to an experimental investigation of the laws of diffusion as applied to the passage of gases through small apertures and multiperforate septa, and ultimately to a complete explanation of the mode by which the diffusive flow can be accelerated by such structures as we find in the leaf, without postulating anything inconsistent with the well-established laws of diffusion; in fact, if

the exact conditions are defined, the degree of efficiency of such a mechanism can be deduced from those very laws.

It is to these and certain other cognate phenomena that I wish to direct your attention this evening, in the hope that my remarks may stimulate further inquiry into a subject of considerable interest, which has many applications in various directions.

That chemists generally in this country have paid far too little attention to diffusion phenomena, and to the important part which they play in many departments of chemistry and biology, is sufficiently evident from the scanty treatment which they have received in the majority of our text-books. This is the more remarkable and less excusable, since the very foundations of our knowledge of the subject were laid down by Thomas Graham, of pious memory, one of the founders and the first President of this Society. If chemists had rendered themselves more familiar with such questions, less surprise would have been expressed when Nernst, as recently as 1904, stated what ought to have been a self-evident proposition, that determinations of the velocities of reactions taking place at the boundaries of heterogeneous systems may be entirely vitiated if we fail to take into account diffusivity as a possible limiting factor.

In this connexion, I should like to refer as briefly as possible to some experiments which I made at the very outset of my inquiries, since they well illustrate this proposition of Nernst.

When a current of air containing any constant proportion of carbon dioxide up to about 18 or 20 parts per 10,000 is caused to move in a turbulent stream of known velocity over the free surface of a normal solution of sodium hydroxide, the temperature being maintained constant, the rate of absorption of carbon dioxide per unit area increases with the speed of the current until a linear velocity of about 260 metres per hour is reached. As long as the other conditions are unaltered, any further increase in the velocity of the air current is unattended by any change in the rate of absorption, the concentration of the carbon dioxide at the immediate boundary of the two surfaces having then attained its maximal value. Until this point is reached, gaseous diffusion is still playing some part in the reaction. That there is no corresponding limitation of the reaction in the liquid itself is shown by the fact that the rate of absorption is not influenced by any further stirring of the solution other than that produced by the air-current passing over it.

Under these conditions, the rate of absorption of the carbon dioxide per unit area of liquid surface varies directly with its partial pressure, and so exact is this relation that it has formed the

basis of a very accurate method for determining the amount of carbon dioxide in the air, which has the advantage that it is quite unnecessary to measure the volume of air employed.

The following table illustrates the degree of accuracy attainable by measuring the rate of absorption per unit area.

The first column shows the carbon dioxide content as given by passing measured volumes of air through a Reiset apparatus, whilst the second column gives the corresponding values deduced from the rate of surface absorption by a known area of the absorbent liquid over which unmeasured volumes of air have been passed in a turbulent stream at a sufficient velocity to produce the maximal effect. The results are given in parts per 10,000 of air reduced to normal temperature and pressure.

TABLE I.

(1).	(2).	Differences.
0·04	0·04	0
0·19	0·19	0
0·56	0·57	+0·01
1·08	1·08	0
1·15	1·21	+0·06
3·21	3·30	+0·09
3·36	3·30	−0·06
4·58	4·41	−0·17
4·89	4·93	+0·04
6·75	6·72	−0·03
7·65	7·50	−0·15
8·54	8·23	−0·31
12·53	12·40	−0·13
17·94	17·74	−0·20

The researches of Graham on the diffusion of gases, commenced in 1829, and continued at intervals up to 1863, are so well known that I need only make a passing allusion to them. They were carried out for the most part with an intervening septum of some porous material, such as plaster of Paris or thin plates of compressed graphite. When the gases communicated through such narrow channels or pipes he was led to a certain generalisation, which in his own words was as follows:

"The diffusion, or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being in the case of each gas inversely proportional to the square root of the density of that gas."

Such results had, of course, only relative values, and Graham clearly saw that absolute values could only be ascertained by allowing the gases to mix through a wide opening by free and unobstructed diffusion. It was only at a much later period that he

commenced any systematic experiments in this direction. He briefly described these in the concluding section of his paper of 1863 on the "Molecular mobility of gases" (*Phil. Trans.*, 1863, 385) with the sub-heading "Interdiffusion of gases without any intervening septum." Beyond showing that whilst a portion of carbon dioxide can diffuse through air at the rate of 7·3 cm. per minute, whilst a sensible portion of hydrogen travels in the same time about five times as far, these experiments did not lead to much, and the numerical results do not lend themselves to a determination of the coefficients of diffusion. Some seven or eight years afterwards, however, they served as a starting point for Loschmidt and his school in establishing a consistent theory of gaseous diffusion.

Long prior to this period Graham had been investigating the diffusion of liquids by his "open jar" method, and in his Bakerian Lecture of 1850 he described a large number of experiments on the comparative diffusivity of different substances in solution. His general conclusions were that, whilst every substance has its own particular velocity of diffusion, the actual rate of transference in solutions of the same substance depends on its initial concentration and on the temperature. Other things being equal, the amount of salt diffused in a given time is very nearly proportional to this initial concentration, and increases with the temperature.

Graham made no attempt to formulate any general law connecting the three variables time, concentration, and space traversed by the diffusate, but his observations fortunately attracted the attention of A. Fick, of Zurich, who, five years afterwards, in 1855, succeeded in developing from them a fundamental law for the operation of diffusion in a single element of space.

Fick's law of diffusion, like Ohm's law at an earlier date, was derived from the principles enunciated in 1822 by Fourier in his celebrated work on the Analytical Theory of Heat—principles which have been found applicable to so many diverse yet analogous sets of phenomena.

Lord Kelvin justly described this treatise of Fourier as a great mathematical poem. Although its beauty and magnificence can perhaps only be adequately and fully appreciated by the mathematician, it is a work of genius which cannot fail to excite the wonder and admiration even of those who, like myself, have not the requisite mathematical knowledge to follow it in all its details.

It was no doubt the ninth chapter of this treatise, dealing with the linear diffusion of heat in rigid substances, which gave Fick the desired clue to his law of diffusion.

Fourier had shown that if we imagine a plane lamina of conducting material with parallel faces, one of which is kept at a constant temperature ϑ_1, and the other at a lower temperature ϑ_2, and sufficient time has elapsed to establish a permanent flow of heat between the two surfaces, then the quantity of heat Q, flowing through the lamina in a given time t, will be directly proportional to the temperature difference $\vartheta_1 - \vartheta_2$ of its two surfaces. Q must also be directly proportional to A, the area of the lamina, and inversely proportional to its thickness x, so that we get the following general expression for the steady condition of the flow of heat:

$$Q = k\frac{\vartheta_1 - \vartheta_2}{x}At.$$

in which k is a quantity dependent on the nature of the substance and representing its conductivity. k is a constant if the conductivity does not vary with the temperature, and may be defined as numerically equal to the quantity of heat which will flow through unit area of a lamina of unit thickness in unit time, when there is unit difference of temperature between the two faces.

If the lamina is supposed to have an infinitely small thickness dx, and there is an infinitely small temperature difference between its two faces, the above expression becomes

$$Q = k\frac{d\vartheta}{dx}A\,.\,dt.$$

$\frac{d\vartheta}{dx}$ is the "gradient of temperature" at any point, so that the flow through unit area per unit time is numerically equal to the *conductivity* multiplied by the *temperature gradient*.

It is the particular merit of Fick that he was the first to express the idea that in all probability diffusion follows the same law, and that, *mutatis mutandis*, it is applicable to the transference of a solute in its solvent, just as Ohm had found it applicable to the flow of electricity in a conductor, the concentration of the solute being in one case the analogue of temperature and in the other of electrical potential.

Proceeding exactly according to the model of Fourier's mathematical development of a linear flow of heat, and assuming that in a diffusive column concentration gradient corresponds with temperature gradient, Fick arrived at the conclusion that when a solute diffuses in an axial direction along a column of constant cross-section, that is, one which is cylindrical or prismatic, the fall of concentration ρ, in any infinitely thin layer, at a distance x from

any point of reference in the column, should in a given time t satisfy the partial differential equation.

$$\frac{\delta\rho}{\delta t} = -k\frac{\delta^2\rho}{\delta x^2}.$$

In this formula k represents the coefficient of diffusivity which, subject to certain limitations, presently to be referred to, is constant for any given solute and solvent as long as the temperature does not vary. It is the exact analogue of Fourier's coefficient of heat conduction.

To quote Fick's own words: "According to this law, the transfer of salt and water occurring in a unit of time between two elements of space with differently concentrated solutions of the same salt must, *caeteris paribus*, be directly proportional to the difference of concentration, and inversely proportional to the distance of the elements from one another."

The law should hold good for any case of diffusion in which the lines of flux are parallel to each other, whether the condition of steady flow has been attained or not, but, owing to the difficulties attending the calculation of a sufficient number of values for the development of the integrals of the equation for special cases, Fick sought the requisite experimental proof in an examination of the distribution of density in a diffusive column which had attained the state of dynamic equilibrium. Under these conditions, the diffusive flux no longer alters the concentration in the space through which it passes, since each infinitely thin layer is receiving as much salt on one side as it is passing on to the next similar layer in juxtaposition.

The above fundamental equation can be shown to contain the proposition that when such a steady condition has been reached, the differences of concentration of any two pairs of strata in the column must be proportional to the distances of those strata, so that the decrease of concentration measured along the axis of the column ought to vary as the ordinates of a straight line.

The experimental method by which Fick attempted to verify this deduction was a somewhat crude one, but the results as a first approximation were found to be in fair accord with theory. Since his time many observers have introduced more refined processes for determining the progressive variations of concentration in a static column, based on optical, chemical, and electrical methods. By far the most satisfactory of these is due to Weber, who in 1879 made use of the fact that the *E.M.F.* developed between two electrodes of zinc or two of copper, immersed respectively in solutions of zinc sulphate and copper sulphate, can be used for measuring with great exactness the concentration at the boundary surface

in contact with the electrodes. The results in every way confirmed the accuracy of Fick's law.

Graham in his last paper on liquid diffusion, published in the *Philosophical Transactions* for 1861, recorded the results of a further series of experiments in which he used an improved method of 'jar-diffusion,' which enabled him to ascertain the degree of concentration of a salt in progressive layers of the diffusion column of a certain definite thickness. He does not refer to the important generalisation of Fick, which was apparently unknown to him, so that his conclusions as regards diffusion velocities are only of relative and qualitative importance. It was not until Stefan in 1879 had submitted these latest results of Graham to mathematical treatment that they were shown to be, on the whole, in accord with Fick's law. That the desired experimental verification should in the first place have been forthcoming from studies on hydro-diffusion rather than from those on gaseous diffusion is not surprising, since, in the latter instance, the molecular interpenetration, which is the essence of the process, takes place with far greater rapidity, and the difficulties in preventing mass movements are correspondingly increased.

Satisfactory proof that the progress of gaseous diffusion can also be expressed by Fick's law was first given by Loschmidt in 1870, the partial pressures of the interpenetrating gases being equivalent to the 'concentration' in hydro-diffusion. As might be expected, the law also holds good for the diffusion of vapours proceeding from the surfaces of volatile liquids.

A full and complete theory of gaseous diffusion from the kinetic point of view has still to be formulated, although so much has been done in this direction by mathematical physicists that there is a reasonable hope that all the observed phenomena will ultimately be deducible from a completed dynamic theory. Be that as it may, however, Fick's law or Fourier's law, whichever we may choose to call it, is one that enables us to solve nearly all the problems met with in practice, and it has the advantage that it is quite independent of any hypothetical assumptions as to the nature, constitution, or molecular condition of the substances taking part in diffusion, provided no dissociation occurs during the process. It merely gives in a compendious and useful mathematical form the experimental relations which exist between the three variables concentration, time, and space traversed in such a manner as to admit of ascertaining the state of the system at any given stage. Like the Phase Rule, it is a theorem which would still remain true even in the unlikely event of our present kinetic and molecular theories being radically modified or entirely abandoned.

The essence of Fick's law is that the 'driving forces' which cause the transference of a substance from regions of high to regions of low concentration are proportional to the concentration gradient.*

Fick's fundamental law, like all other "laws," has its limitations and must be regarded merely as a close approximation to the truth, and subject to correction as our knowledge increases. As it stands it may be compared with the uncorrected gas law of Boyle connecting pressure with volume. It assumes, for instance, that the coefficient of diffusion, k, at a given temperature is constant and independent of the concentration, which is certainly not strictly correct.

In his "Kinetic Theory of Gases," O. E. Mayer, in attempting to deduce the theoretical formula of gaseous diffusion from the kinetic considerations of Maxwell and Stefan, indicates that whilst the dynamical theory is in accordance with observation as far as the influence of temperature and pressure is concerned, his dynamic formula suggests that k, the diffusivity coefficient, ought to vary slightly with the number of molecules of one or the other kind of gas in unit volume of the mixture; that is to say, it ought to assume a somewhat different value in different parts of a diffusive column, dependent on the ratio of mixture.

Small progressive variations of this kind have been recently recorded by Jackmann, Deutsch, Schmidt, and Lonius for the free interdiffusion of various pairs of gases, but it is questionable whether the very small differences recorded are not within the limits of experimental error (see Jean's "Dynamical Theory of Gases," p. 334). Moreover, these experiments were necessarily conducted with the two gases initially at equal pressures, and therefore containing the same number of molecules per unit volume. O. E. Mayer has pointed out that these are not the best conditions for ascertaining if k varies with the ratio of mixture, and that we ought to employ gaseous mixtures containing only small masses of one of the constituents.

* It is somewhat surprising that the phenomena of osmotic pressure have not been often regarded from this point of view.

It is as legitimate to speak of the concentration of the *solvent* in a solution as the concentration of the *solute*, both are expressed by $\frac{\text{mass}}{\text{volume}}$. As the concentration of the solute increases that of the solvent diminishes. When a solution and the pure solvent are separated by a membrane impervious to the solute the inequality of "concentration" of the solvent on either side of the membrane must necessarily result in a diffusion current passing across the membrane from the region of high concentration of the solvent to regions of low concentration, that is, from the pure solvent to the solntion. It is this process which gives rise to the "osmotic pressure."

During a certain stage of my work, I have been able to realise these conditions by determining the rate of the diffusive flow of atmospheric carbon dioxide, at a partial pressure of about 3/10,000 of an atmosphere, along a column of air after the static condition had been induced by introducing a perfect absorber of the carbon dioxide at one end of the tube.

If the coefficient of diffusivity for the system carbon dioxide–air is appreciably influenced by the ratio of mixture, these are just the conditions under which one would expect indications of it.

In these experiments, and in others made by determining the rate of flow through apertures of known dimensions, no positive evidence of any such differences was forthcoming (see Brown and Escombe, *Phil. Trans.*, 1900, [*B*], **193**, 241, 269).

In the phenomena of hydro-diffusion there is more convincing evidence that the value of k appreciably varies with the concentration, but until we have more accurate determinations of the coefficients of diffusivity of solutes than at present, this and other small disturbing influences, such, for instance, as those due to volume changes induced by the progressive dilution of the diffusate, cannot be evaluated with certainty.

Meanwhile, Fick's law is a very good approximation and sufficient for all ordinary purposes. It only requires correction in the same manner as does Fourier's law in the theory of heat-conduction: "as there the quantity of internal conduction slowly diminishes as the temperature rises, so here the quantity of the diffusion gradually sinks to smaller values as the concentration increases; Fick's hypothesis expresses the course of diffusion with only the same accuracy with which Fourier's elementary law represents the process of the conduction of heat in rigid bodies" (Weber).

I must now pass on to the consideration of some concrete examples of diffusion in certain typical and well-defined systems.

I have already referred to some of the conditions which exist in a diffusion column of cylindrical or prismatic shape when the concentrations of the diffusing substance are maintained at constant but unequal values at its two faces for a sufficient length of time to induce the steady condition of flow from one face to the other. In such a system, equal amounts of the diffusate must necessarily pass across each cross-section in equal intervals of time, and the fall of concentration of the diffusate will be uniform; that is to say, if the densities or concentrations are plotted against the corresponding distances of the cross-sections from the point of origin, the slope or gradient of density will be represented by a right line

the steepness of which is inversely proportional to the total length of the column.

If the concentration at one face is represented by ρ, that at the other face by ρ_1 some value which is less than ρ, and the length of the column by L, then at constant temperature the magnitude Q of the flux will vary directly as the gradient $\frac{\rho-\rho_1}{L}$. Q will also be directly proportional to the area of the cross-section of the column, to the coefficient of diffusivity k, and to the time t.

If consistent units are employed, the diffusive *efficiency* of the system will be represented by the equation

$$Q = k\frac{\rho-\rho'}{L}At.$$

In such a static system the stream lines of the flux will be represented by an infinite number of straight lines drawn parallel to the axis of the column. On the other hand, every cross-section of the column corresponds with a surface of equi-density of the diffusate to which the lines of flux are normal, and the uniformity of the gradient may be illustrated by drawing any number of lines representing these surfaces of equi-density at equal distances apart.

Although the essential elements of the system have their analogues in the conduction of heat in a bar which has attained the steady state, the parallelism of the two sets of phenomena is only complete if we imagine such a bar to possess no power of thermal emission from its surfaces.

On the other hand, the diffusive flow is strictly analogous to the steady flow of electricity along a conductor of uniform cross-section maintained at its two ends at a constant difference of potential $V - V_1$. In this case, the coefficient of diffusivity, k, corresponds with the electrical conductance, and the surfaces of equi-density with those of equi-potential.

Some time ago Professor Hele Shaw (*Phil. Trans.*, 1901, [*A*], **95**, 303), while investigating the stream lines of a moving viscous film, which is known to obey Fourier's law, discovered that two-dimensional cases of magnetic lines of force can be illustrated in a very beautiful manner by the flow of differently coloured viscous liquids under a constant head of pressure. In a diffusive field, it has not been found practicable up to the present to demonstrate the existence of the actual lines of flux, but, on the other hand, it is quite possible to render visible the surfaces of equi-density of a diffusate, and from these to deduce the shape of the stream lines which are everywhere orthogonal to those surfaces.

In the early days I obtained visual evidence of the shape and

relation of the zones of equi-density in various systems by the intermittent diffusion of solutions of sulphates and chromates into a gel of agar or gelatin to which had been added a little barium chloride. In this way, the surfaces of equal concentration are self-delineated by the progressive bands or zones of the insoluble barium salts precipitated within the gel (see Fig. 1). Latterly for this purpose I have availed myself of the Liesegang phenomena, whereby, under favourable conditions, two opposing diffusive streams of reacting substances can be made to produce in the gel a rhythmical series of zones and bands which follow the contours of surfaces of equi-density.

I have here some examples which show the position of these surfaces as they exist in cylindrical and prismatic diffusion columns.

In hydro-diffusion, most of the coefficients of diffusivity which appear in our tables of physical constants have been derived from the observed rate of flow in columns which have attained the steady condition to which I have referred. The values of k are generally expressed in centimetre-gram-day units, reference being made to the temperature and the concentration of the solution at the head of the column. Many of the recorded values are only approximations, and have to be treated accordingly. The static method is only rarely applicable to gases, but in a modified form I have shown that it can be successfully employed in determining the diffusivity of atmospheric carbon dioxide in the mixed gases of the air, although its partial pressure is so small.

We have seen that as long as we confine ourselves to the study of diffusive columns which have attained the steady condition of flow, the relations of the various factors which determine the rate of flow and the distribution of density in the column are capable of simple mathematical treatment. If, however, these conditions are not completely fulfilled, and the diffusate is still in process of extension into fresh regions of the column, the particular state of the system can no longer be determined by elementary mathematics, but nevertheless can be deduced from the fundamental equation of Fick when certain definite information is forthcoming as to the conditions of the experiment.

I have here a cylindrical column of agar gel down which is diffusing dilute hydrochloric acid, the concentration of which is maintained constant at the upper face of the column. To this gel has been previously added a little Congo red, and the degree of penetration of the acid is marked by the progressive change of colour from red to blue.

Since the acid diffusate is constantly advancing further and

further from its source, it is evident that any given stratum in the blue part of the column must be receiving more of the acid on its upper surface than it is transmitting from its lower surface to the next similar stratum immediately below it, so that the fall or gradient of density of the diffusate cannot be uniform, as it is in a diffusive column which has attained the static condition. A complete definition of the state of such a system at any desired moment is, however, derivable from the partial differential equation of Fick if we have some means of determining the exact position in the advancing column of a definite and thin stratum where the concentration of the diffusate has a known small value, and we can measure the distance between this stratum and the face of the column, where the acid is maintained at a known concentration.

The extreme limit of the blue coloration corresponds with such a definite stage, and the concentration at this point can be ascertained by a preliminary titration experiment. Knowing the length of the blue column, the ratio of the two concentrations, and the time the experiment has lasted, we have all the elements requisite for calculating the distribution of density in the column and the value of k.

I am indebted to Sir Joseph Larmor and to Mr. R. A. Fisher for a complete mathematical treatment of this problem, which is practically identical with that of a cooling Earth as investigated many years ago by Lord Kelvin. I need not trouble you with the equation which fits all the required conditions, and will only remark that the calculations are much facilitated by the fact that the equation involves the Probability Integrals of the Normal Curve of Errors, which has been thoroughly tabulated, and is much needed in the Theory of Gases.

One of the conclusions reached during the mathematical analysis is that if a succession of observations are made on such an advancing column of diffusion, the time t requisite for the extension of the blue coloration along the axis ought to be directly proportional to the square of the length x, measured from the free surface of the gel, so that $\frac{x}{\sqrt{t}}$ ought to be constant for all times. How closely this deduction accords with direct experiment will be noticed from the following results, obtained in the diffusion of dilute hydrochloric acid under the described conditions.

Time in hours. t.	Length of blue column. x.	$\frac{x}{\sqrt{t}}$.
1·0	8·0 mm.	8·00
3·0	14·0 „	8·08
5·5	19·0 „	8·10
7·41	22·0 „	8·08
18·0	34·0 „	8·01
*24·0	40·0 „	8·16

* By this or some similar method it is quite possible to determine how k, the coefficient of diffusivity, varies with the initial concentration of the solute at the face of the column.

So far, we have been considering systems in which the stream lines of the diffusive flux are parallel to each other and to the sides of a containing vessel which is cylindrical or prismatic in form. We have seen that in such cases, when the steady condition of flow has been attained, the gradient of density of the diffusate is uniform from end to end of the column, and that this uniformity of gradient can be illustrated by drawing at right angles to the axis, and at equal distances apart, a series of lines corresponding with the surfaces of equi-density. This uniformity of gradient no longer holds good, however, if the stream lines are rendered *convergent* or *divergent* by suitable means.

Suppose, for instance, we have a steady diffusive flow taking place along a tube having the form of a truncated cone. In those regions where the stream lines are more crowded together, that is to say, in the narrower part of the tube, the gradient of density is greater than it is in the wider part. If, therefore, we desire to illustrate this as we have done for the cylinder, we have to draw the lines corresponding with equal decrements or increments of density closer and closer together as the narrower end of the tube is approached.

For a given difference of "diffusion potential" between its two ends, the actual "efficiency" of a conical tube is calculable if we know the length of the truncated cone, its solid angle, and the particular value of k for the diffusing substance, but as this is only a special case deducible from diffusion around a sphere, which we shall presently consider, I will not dwell on it further except to compare the relative efficiency of a truncated cone and that of a cylindrical tube of the same length which has a uniform cross-section equal to that of the smaller end of the conical tube. This difference may be illustrated by a concrete example.

Suppose we have a truncated cone of 10 cm. in length, the smaller end of which has a spherical area of 1 sq. cm. at a distance of 1 cm. from the apex of the completed cone; then it can be shown that under similar conditions the diffusive flow ought to be *eleven* times greater through the conical tube than through a

cylindrical tube of the same length with a uniform cross-section equal to that of the smaller end of the conical tube.

Such accelerations of the diffusive flow through conical tubes can be readily verified experimentally in various ways. The principle is one which must have an important application in the respiratory organs of air-breathing animals, especially in the alveolar and higher regions of the lungs which lie beyond the influence of the tidal air, and in which the interchange of gases is dependent solely on diffusion.

When a body of spherical shape capable of acting as an absorber or an emitter of a diffusible substance is suspended in a field which is free from convection currents, the direction of the flux, to or from the sphere as the case may be, will be represented by a series of lines drawn radially from its centre, and the surfaces defining regions of equal density of the diffusate will form a series of external shells concentric with the sphere.

Let us first consider a sphere which is acting as an absorber in a practically infinite diffusive field in which the initial concentration has some fixed value represented by ρ, and that a sufficient time has elapsed to induce the steady condition of flow. We will also assume that the sphere is a perfect absorber, that is to say, that at its immediate surface the concentration of the diffusate is always maintained at zero. Under these conditions, the concentration of the diffusate around the sphere will vary from zero at its immediate surface to a value which is practically ρ in some region remote from the sphere.

Strictly speaking, ρ is a limiting value which theoretically is never reached, but for practical purposes it may be regarded as attained at distances exceeding ten diameters of the sphere, so that similar spheres at this distance apart would exercise very little interference with each other.

The distribution of the density or concentration of the diffusate around the sphere will be such that, proceeding from its surface outwards in a radial direction, the defect of density, represented by $-\rho$, will vary inversely with the radial distance from the centre of the sphere. Thus at radii 1, 2, 3, 4 . . . the negative densities will be represented by $-\rho, \frac{\rho}{2}, -\frac{\rho}{3}, -\frac{\rho}{4}, \ldots$, whereas the actual positive densities, measured in the same direction, progress as 0, $\frac{1}{2}\rho, \frac{2}{3}\rho, \frac{3}{4}\rho \ldots$

At a distance of, say, 20 radii, the diffusate will consequently have a concentration of $\frac{19}{20}\rho$, or within 5 per cent. of the limiting value.

In a system such as this (the steady condition of flow being postulated), it is evident that during any given time interval equal amounts of the diffusate pass through each one of any number of concentric shells of equi-density described around the acting sphere. Since the surfaces of spheres are proportional to the square of their radii, this equality of flow implies that if we compare any two of the shells, the flow through unit area in each case must be inversely proportional to the squares of the radii. The flow per unit area is, however, directly proportional to the gradient of density, so that in such a field of diffusion as we are considering the gradient of density, that is to say, the fall of density per unit of radial length, must everywhere be inversely proportional to the square of the radius.

This leads to the conclusion that if we have two spheres of different dimensions acting as perfect absorbers in the same field of diffusion, and they are placed at such a distance apart as not to interfere with each other sensibly, then their relative *efficiencies*, as defined by the amount of diffusate which they will absorb in a given time, are not proportional to their surfaces, but to their linear dimensions. Thus a sphere of double or half the unit radius will absorb in a given time double or half the amount of diffusate.

If we represent the "efficiency" of an absorbing sphere by Q, its radius by r, the maximal concentration of the diffusate at some remote point by ρ, and the coefficient of diffusivity of the substance by k, we get the following general expression, which, *mutatis mutandis*, is also applicable to an emitting sphere when the steady condition is reached:

$$Q = 4\pi r\rho k.$$

If the sphere is not a perfect absorber and the diffusate has some ascertainable concentration at its surface, represented by ρ_1, then we should have to substitute $\rho - \rho_1$ for ρ in the above equation.

It will be noted that the phenomena of steady diffusion around a sphere are strictly analogous with those exhibited by a freely suspended and insulated spherical conductor which is electrically charged. The concentric shells of equal density of the diffusate correspond with the shells of equipotential in the dielectric surrounding the charged sphere, whereas the gradient of density measured along the lines of flux corresponds with the gradient of potential around the charged sphere measured along the lines of force. Moreover, what we have termed the 'efficiency' of the diffusive sphere is the exact analogue of the electrostatic *capacity*, both varying directly with the linear dimensions of the sphere.

If in spherical diffusion we describe a series of the concentric

shells of equal density at the appropriate intervals corresponding with equal increments or decrements of density, according to whether the sphere is absorbing or emitting, we obtain a figure which also represents the relative position of the equipotential zones around a charged sphere for equal differences of electrical potential, and in a gravitational field the relative position of the zones corresponding with equal differences of gravitational force.

Further striking and interesting analogies between the electrostatic and diffusive phenomena come to light if we study the lines of force and the equipotential surfaces around two spheres charged to the same electrical potential, and compare these with the surfaces of equi-density and the corresponding lines of diffusive flow induced in a diffusive field by two emitting spheres sufficiently close together to interfere with each other's action.

I will first show you the theoretical disposition of the surfaces of equipotential around two spheres charged to the same potential with electricity of a similar kind.

This illustration (Fig. 2) is taken from a drawing given by Clerk Maxwell in his "Electricity and Magnetism." For the sake of simplicity, I have omitted the actual lines of force, which in this two-dimensional projection would in all cases be normal to the equipotential lines. The forms taken by these lines or surfaces were the result of laborious calculation.

I will now show you (Fig. 3) how in the case of diffusion through two circular apertures the analogous surfaces of equi-density of the diffusate can be self-delineated by the interaction of the stream lines radiating from and to the apertures, thus giving a sectional representation of the shells of equi-density around spheres of corresponding diameters, set at similar distances apart in the same diffusive field. In the particular case shown on the screen, the interfering rings were produced by intermittent diffusion of alkaline sulphates and chromates into a gel containing a little barium chloride. Similar phenomena on a small scale can also be produced by the interference of two sets of Liesegang's rings formed by the diffusion of a solution of lead nitrate through two small apertures in a thin plate of celluloid floated on an agar gel containing a little potassium iodide. Examples of this are before you.

In such a system, however produced, the reacting substances travelling in opposite directions mark out regions of equal concentration of the diffusates, the true stream lines being orthogonal to these surfaces.

It will be noticed, in the first place, that in the early stages of their formation the rings lie closer together around the smaller than around the larger aperture, just as is the case with the zones

FIG. 1.

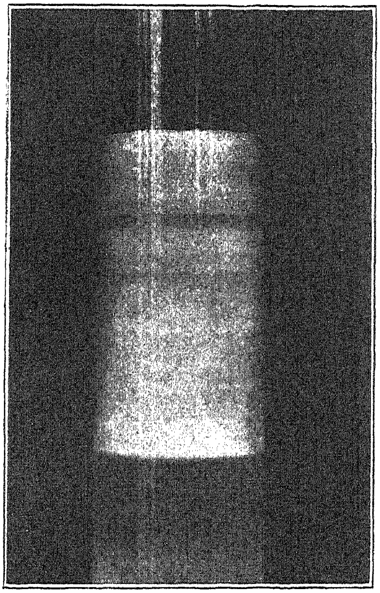

FIG. 2.

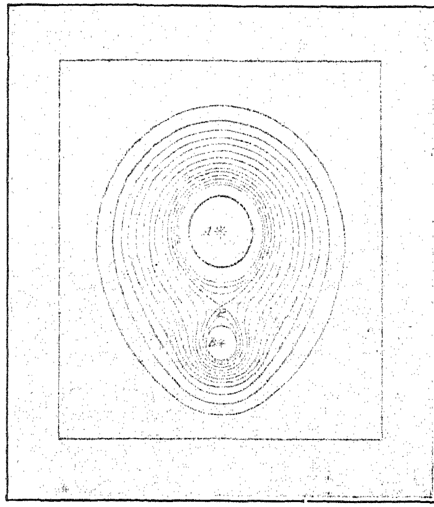

FIG. 3.

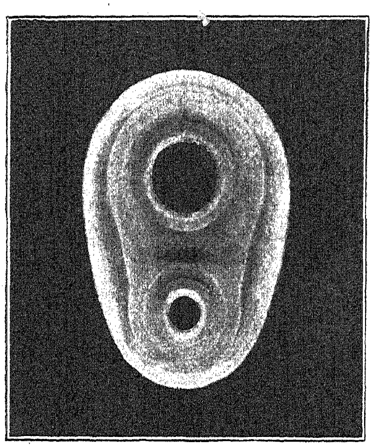

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FIG. 4.

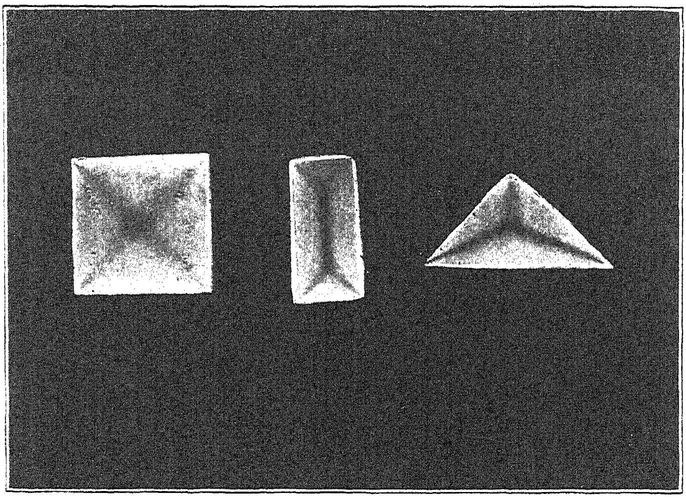


FIG. 5

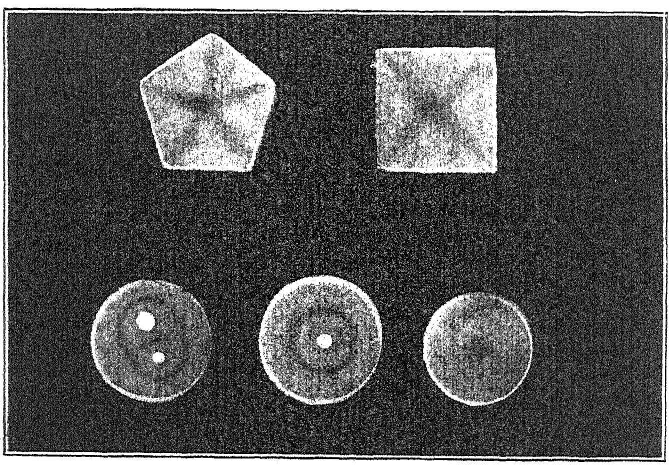


Fig. 6.

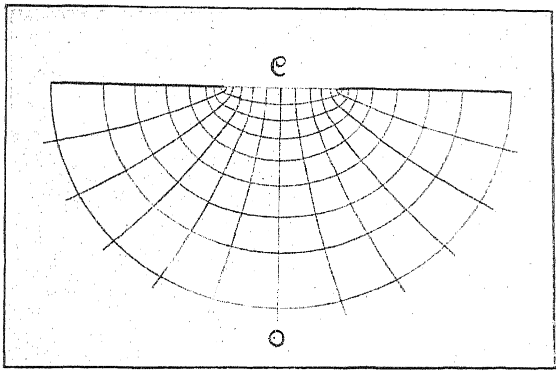


Fig. 7.

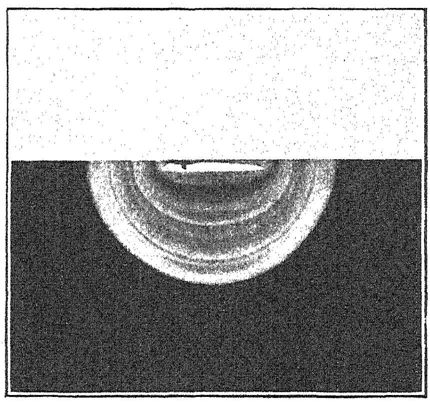


Fig. 8.

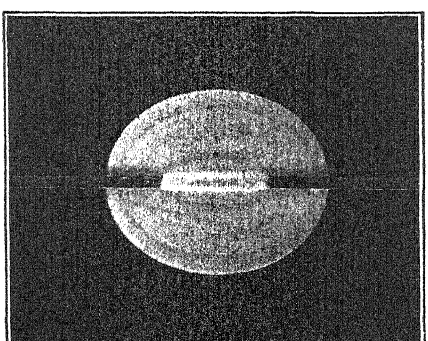


FIG. 9.

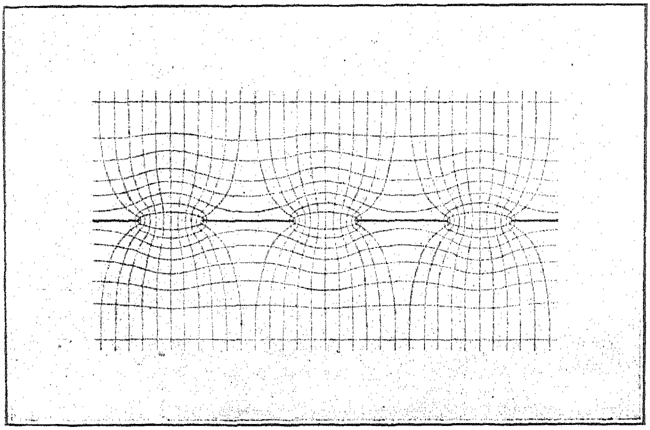


FIG. 10.

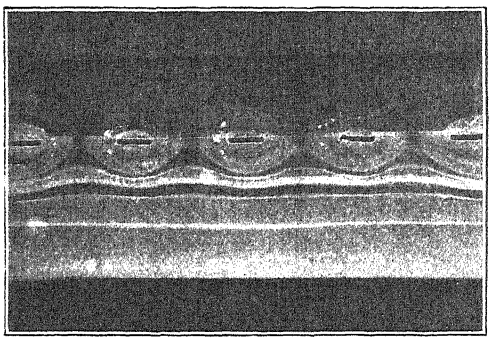
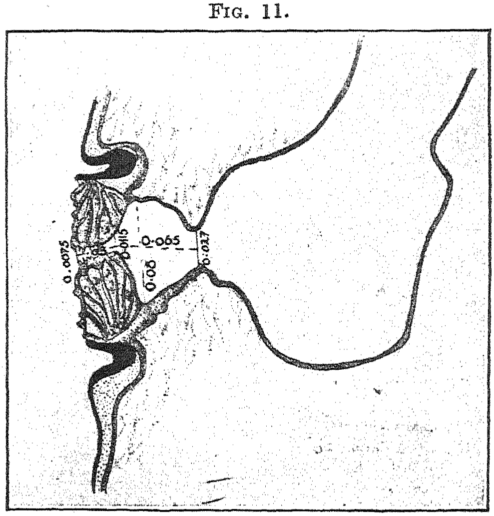


FIG. 11.



of equipotential around two spheres of unequal size electrically charged to the same potential.

As the divergent stream lines of diffusion progress, they begin to interfere with each other, and the rings to which they are normal begin to change their shape, ultimately fusing into a single system similar to the equipotential lines of Clerk Maxwell (see Fig. 2).

The diffusive and the electrostatic systems correspond in every detail. Maxwell by his laborious graphical method showed that if any one of the lines of the combined system is regarded as defining the surface of a single body (which in this case would have the shape of a dumb-bell with one end larger than the other), the equipotential surfaces come closer together at the smaller end, further apart at the larger end, where the curvature is less, and furthest apart of all in the centre of the dumb-bell, where the curvature is negative, the relative nearness of the lines indicating the relative density of the charge at these points.

You will see all this well exemplified in the analogous diffusive system. Where the surface curvature is greatest, there the equidensity lines lie closer together, thus indicating a higher gradient of density in these regions and a greater diffusive flow per unit area.

You will also observe, and perhaps this is the most interesting point of all, that Maxwell marks a certain region (P, Fig. 2) in the line joining the centres of the electrified spheres, which he states is a point of equilibrium, and that the surface density on a body of the form of this surface would be zero at this point.

This region of equilibrium is also defined in the diffusion figures of Fig. 3 as one of no precipitation; it is, as it were, a "dead spot."

If we fill a tube open at both ends with a gel containing a little barium chloride and then immerse it in dilute sulphuric acid, precipitation of barium sulphate progresses equally from either end of the tube until its centre is approached. There is, however, always a narrow central zone in the middle of the tube which remains clear, no matter what the terminal concentration of the acid may be or how long the experiment has lasted. The same thing occurs when the diffusion of the acid takes place centripetally from the edges of a circular glass cover-glass placed over a drop of the same gel placed on a glass slide, but in this case the dead space takes the form of a circular spot.

The explanation is that the two reacting substances, the sulphuric acid and the barium chloride, are diffusing in opposite directions, and that the barium ions have been depleted from the equilibrium zone before the acid reaches it, a fact which is readily demonstrated

by extruding the column of gel from the tube, dividing it in the centre of the 'dead' region, and applying a little sulphuric acid to the cut ends. When a diffusible coloured substance is employed in solution, the same phenomenon is observed at first, but ultimately, as might be expected, the column shows an equal distribution of colour throughout.

There is a further analogy to certain acoustic phenomena which is not without interest. The dead space in a tube such as I have described corresponds in position with that of the node of an open organ pipe when it is sounding its fundamental note. This analogy may be carried still further. If, for instance, inward diffusion takes place simultaneously from all the four edges of a square cover-glass, the four opposing streams of the reacting diffusates mark out the regions of equilibrium in the form of a regular cross with its arms directed towards the four corners of the square, thus producing an exact picture of the well-known Chladni's figure which marks out the nodes of a square vibrating plate bowed at the centre of one of its edges.

By varying the shape of the plate, a further instructive series of interference diffusion figures can be obtained, of which a few examples are given (see Figs. 4 and 5). On the table are further illustrations of somewhat similar figures produced by Liesegang rings of lead oxide. By suitable arrangement, it is possible to imitate the stratification of natural agates in this manner.

Before leaving the subject of spherical diffusion, I must dwell for a moment on the application of its principles to certain chemical and biological problems.

We have seen that in a diffusive field the actual "efficiency"* of a sphere, functioning as an absorber or emitter of the diffusate, varies directly with the radius of the sphere. Hence it follows that if a sphere is divided into any number of spheres n, of equal volume, and these are distributed in a similar field at such distances apart as not to interfere with each other, then the increased efficiency of the divided system will be represented by $n \cdot \sqrt[3]{\frac{1}{n}}$, when that of the original sphere is taken as unity. On the other hand, the increase in surface will only be represented by $\sqrt[3]{n}$, so that the 'efficiency' increases as the square of the surface.

For instance, if a sphere of unit volume is subdivided into 1000 equal spheres, the surface extension over that of the original sphere

* The 'efficiency' denotes the rate of emission or absorption for a unit or standard difference of concentration, and is analogous to the electrical capacity of a similar spherical conductor, that is, the charge held for unit difference of potential.

will be represented by 10, whilst the diffusive 'efficiency' of the whole subdivided system will be represented by 100.

The influence of a solid catalyst in increasing the velocity of a chemical reaction, such as that induced by a metal in the 'colloidal' state, is generally attributed to previous adsorption and condensation of the substrate on the surface of the particles.

Let us assume that the particles of the catalyst are spherical, and that the adsorption of the substrate at the boundary of the two phases has to attain a certain small value, which we will call the critical value, before the reaction starts, and, further, that the rate at which the chemical change takes place from this point is practically infinite.

Under these conditions, in order to maintain the rate of change appropriate to the concentration of the substrate in the main body of the liquid, we must retain the concentration at the surface of the particles at its critical value.

If these particles exceed a certain size, this will necessitate more or less vigorous stirring of the liquid. The smaller the particles become, however, the more nearly they will be able to maintain the critical concentration at their surface by diffusion alone, owing to the increasing convergence of the diffusive stream lines producing an ever increasing gradient of concentration. A point will ultimately be reached at which stirring will produce no increased effect.

It has often been assumed that the effect produced by subdivision of the catalyst under these conditions is directly proportional to the area of the surface, but it is evident that under appropriate conditions the activity of a unit mass of a catalyst must vary, not with the surface, but with the *square* of the surface.

These same principles enable us to understand how it is that minute dimensions confer advantages on certain micro-organisms in carrying out their life processes of nutrition and the correlated processes of fermentation and putrefaction.

When these organisms have little or no power of locomotion and the media in which they live have a low degree of mobility, they must be largely dependent on diffusion for the access of material from their surroundings and for the removal of the products of change from their immediate neighbourhood.

Minuteness of dimensions favours these convergent and divergent streams and enables the organism to supply its requirements from a medium of a much lower concentration of substrate than would be the case if the cell were of larger dimensions, thus exemplifying the "importance of being little"—and remaining so (see Slater and Sand, "The Rôle of Diffusion in Fermentation by Yeast Cells," T., 1910, **97**, 922).

Did time allow, I could give further examples of the applications of these same principles to diverse processes in which diffusion plays a more or less prominent part. They are, for instance, operative in the ignition of finely-divided pyrophoric substances, in the sparks produced by flint and steel, and in the rapid propagation of combustion of coal dust and other fine organic substances suspended in air.

We are too apt to regard diffusion as being necessarily a slow process, especially in liquids, which is by no means the case if the gradient of density is enhanced by the extreme convergence of the lines of flux on any particular point.

We have seen how the self-described diffusion figures surrounding two emitting spheres brought into each other's neighbourhood correspond in every detail with Clerk Maxwell's lines of equipotential and lines of force around two similar spheres charged to the same potential with the same kind of electricity.

The diffusion experiment may be so varied as to cause one of the circular perforations, corresponding with the sections of the spheres, to act as an emitter and the other as an absorber or 'sink' of the diffusate.

Under these conditions, the lines of equi-density of the diffusate tend to arrange themselves in accordance with Maxwell's figure of the equipotential lines around spheres, one of which is charged with positive and the other with negative electricity.

It is impossible to regard these analogous phenomena without suspecting that there is also a similarity in the dynamic relations of the two systems. We are, for instance, led to inquire whether in the case of diffusion there are any unbalanced forces which tend to move the bodies in a diffusive field.

I have recently referred this problem, which appears to present great difficulties, to Mr. R. A. Fisher, who is still at work on it. Whatever the final results of his analysis may be, it appears that if a small, elongated body which has a differential power of absorption at its two ends is introduced into a diffusive flow, it will tend to set itself along the lines of flux and to head up stream with its less absorptive end facing the region of the higher concentration of the diffusate.

If this deduction is correct, as I have but little doubt it is, it contains a physical explanation of certain phenomena of chemotaxis which have always been a great puzzle to the biologist. Let me give an example of what I mean.

The fertilisation of the non-motile egg-cells of the ferns and mosses is brought about by free-swimming, highly motile spermatozoids, which crowd into the archegonia in such a manner

as to suggest that there is some emission of an attractive substance from the opening which gives the needed directive force to the spermatozoids.

By immersing the free end of a fine capillary tube charged with a very dilute solution of sucrose into water containing the free-swimming spermatozoids of a moss, Pfeffer was able to demonstrate that whereas the movement of the spermatozoids in the body of the liquid occurred indifferently in all directions, it assumed a unidirectional character in the immediate neighbourhood of the orifice from which the sugar was diffusing, and the organisms crowded into the tube, which acted as a sort of artificial archegonium. Similar chemotactive movements also occur with the spermatozoids of ferns when the capillary is filled with an extremely dilute solution of malic acid. Under certain conditions, the movements are reversed in direction, when the chemotaxis is said to be *negative*. Somewhat similar movements have also been observed in certain motile bacteria, which are "attracted" to regions in which an evolution of oxygen is taking place within the cells of algæ containing chlorophyll and suitably illuminated.

Such movements, which at first sight appear to indicate a certain degree of intelligence on the part of the organisms, are, I believe, capable of a very simple physical explanation, which is at any rate worth serious consideration.

It must be borne in mind that in all such cases the real driving force of the spermatozoid or bacterium is supplied by its own motile organs, the flagella; all that we are called upon to explain is the origin of the *directive* force which is exercised when the organism finds itself in a suitable diffusive field in which the gradient of concentration of the diffusing substance is varying in a certain determinate direction.

Such a directive influence will certainly be exerted if the motile organism can act as an *absorber* of the diffusate, and this power of absorption is not uniform over its surface owing to a variation in the degree of permeability of the investing cell-membrane.

If those portions near the 'head' of the spermatozoid are less permeable to the diffusive substance than those nearer the flagellum in the rear, we should expect the organism to orientate itself in such a manner as to head towards the region of higher concentration—that is to say, towards the point of origin of the diffusive flow. This would correspond with the conditions of *positive* chemotactic movement. If, on the other hand, the region of the cell-membrane is more permeable at the front than at the rear, we should expect to get a heading down stream and a consequent re-

cession from the point of origin of the diffusate, that is, *negative* chemotaxis.

We have seen that when two perfectly absorbing spheres of different dimensions are suspended in the same diffusive field at a sufficient distance apart to exert no practical influence on each other, we should expect the ratio of their "efficiencies" as absorbers would be the same as the ratio of their electrostatic capacities when once the steady condition of diffusion has been induced. This should be equally true of bodies of any shape, so that if by experimental or other means both the electric capacity and volume of the body are known, we can by analogy determine its diffusive efficiency in a given field by referring it to that of a sphere of equal volume.

In the case of freely suspended spheres, the experimental verification of this proposition presents certain difficulties, which can, however, be avoided by a further simplification of the problem, as follows:

Clerk Maxwell has shown how it is possible to calculate the electric capacity of a planetary or oblate spheroid, which is formed by the revolution of an ellipse around its minor or polar axis, and to refer this capacity to that of a sphere of unit radius. Now a circular disk may be regarded as a particular and extreme case of a planetary ellipsoid in which the minor or polar axis has vanished. Such a disk if embedded flush in a non-conducting material has an electrostatic capacity of $\frac{1}{\frac{1}{2}\pi}$ times that of a sphere of the same radius. Hence, if the analogy really holds good, we should expect the "diffusive efficiency" of a disk to be represented by

$$\frac{4\pi kr\rho}{\frac{1}{2}\pi} = 8kr\rho,$$

if we count both sides of the disk, or $4kr\rho$ if the disk is absorbing or emitting on one side only.

We may substitute for such a disk a circular aperture in a very thin diaphragm through which diffusion is allowed to go on under well-defined conditions.

In these circumstances, by measuring the rate of flow of atmospheric carbon dioxide or of water vapour through circular apertures of known dimensions into a suitable vessel which ensures its absorption on the other side of the diaphragm, I have been able to obtain very complete evidence that experience and theory are in accord. Moreover, it is easy also to demonstrate that the rate of diffusive flow is directly proportional to the linear dimensions of

the aperture, not to its area. In fact, all the observed phenomena in their quantitative relations are strictly in accordance with those deducible from the application of the electrostatic analogy.

By using a method of this kind, it is quite possible in some cases to determine with considerable exactness coefficients of diffusivity, and it was in this manner that I was enabled to determine the value of k, the coefficient of interdiffusion of carbon dioxide and air, for dilutions of carbon dioxide representing about 3/10,000 of an atmosphere.

The conditions of evaporation in still air from a circular surface of liquid surrounded by a wide rim were mathematically investigated by Stefan in 1881, who also made use of the electrostatic analogy.

He concluded that the rate of evaporation in perfectly still air ought to be proportional to the linear dimensions of the liquid surface, and not, as was commonly supposed, to its area. Further, his analysis indicated that the divergent lines of flux of vapour emitted from the surface ought to be represented by a series of hyperbolas having their common foci in the bounding edge of the circular surface, whilst the curved surfaces of equal partial pressure of the vapour overlying the disk should form an orthogonal system of ellipsoids, also having their foci in the edge of the disk. Since these ellipsoids, conforming to surfaces of equal partial pressure, necessarily come closer together at the margin of the disk than towards its centre, Stefan concluded that, under the conditions postulated, evaporation proceeds more rapidly at the edge than at the centre.

Such a system is illustrated in a reversed position in Fig. 6, which also represents equally well the distribution of the lines of force and surfaces of equipotential in the neighbourhood of a circular electrified disk embedded flush in a wide, non-conducting rim.

I am not aware that Stefan or his successors ever attempted to verify his deductions by actual experiment. I am able this evening to show you how this can be done.

In the first attempts made by my colleague, Mr. F. Escombe, and myself, we used a rectangular glass cell divided horizontally by a plate of celluloid having a circular hole punched through it. The lower half of the cell was completely filled with a gelatin gel containing a little barium chloride, and the upper half with a solution of alkaline sulphate. The opposing streams of the reacting diffusates produced in the gel in the neighbourhood of the aperture an opaque spheroidal figure which changed its shape as it became larger. By photographing this at intervals and super-

imposing the negatives, it was seen that the limiting surfaces of the constantly changing figure marked out by the precipitation of the barium sulphate conformed exactly to the system of ellipsoids demanded by theory.

The process was further improved by the intermittent diffusion of sulphates and chromates through the aperture, thus forming a banded structure in the gel, well seen when the block of gelatin was divided by a vertical section. This further led to employing a semicircular aperture with its flat side coincident with the plane of one of the sides of the glass vessel, so that the arrangement of the banded structure on the diffusion spheroids was visible in cross-section through the glass. Further developments led to the use of narrow slits cut in a thin plate of celluloid which formed one side of a thin, rectangular cell filled with the gelatin–barium mixture. Such a slit manifestly corresponds with a vertical central section of a circular disk looked at edgeways.

In the slides now before you (Figs. 7 and 8) you have a photographic reproduction of such a system of the shells of equi-density in the immediate neighbourhood of the opening through which the diffusion is taking place. It will be noted that their shape and disposition are exactly those predicted by Stefan, the alternate zones of barium sulphate and chromate forming a series of confocal ellipsoids having their foci in the edges of the disk, and therefore approximating more and more to the spherical shape as we progress outwards. It is also to be observed that the ellipsoidal shells come closer together at the edges than in the centre, indicating that in these regions the gradient of density is greater, and consequently that the flow per unit area is also greater.

It must not, however, be supposed, as I have sometimes seen it stated, that the acceleration of diffusive flow produced by small apertures is dependent merely on this increased flow at the edges. There would be almost the same amount of acceleration if the equi-density zones could be imagined to be spherical instead of ellipsoidal. The acceleration of flow per unit area as the size of the aperture is diminished is conditioned in the main by the degree of convergence or of divergence of the lines of flux. The smaller the aperture, the greater becomes this convergence and divergence, with a corresponding increase in the gradient of density in its immediate neighbourhood.

The experimental study of diffusion through single apertures naturally leads up to a consideration of the effects to be expected from a series of small apertures in a thin diaphragm when such a multi-perforate septum is inserted in a line of diffusive flow.

One would expect, from what has been said, that if the apertures are small and arranged at suitable distances apart, the accelerated flow induced by each individual aperture would to a large extent neutralise the effect of the obstruction produced by the imperforate parts of the diaphragm, and that under favourable conditions the intervention of such a septum would not sensibly diminish the rate of flow in the diffusive column, although the aggregate area of the openings might be small as compared with the cross-section of the column.

This was actually found to be the case. As an instance, I may mention an experiment in which a thin film of celluloid perforated with 100 circular apertures per sq. cm., each one of a radius of 0·19 mm., produced no sensible effect in obstructing the static diffusion of atmospheric carbon dioxide down a column of air, although the imperforate parts of the septum blocked out nearly 90 per cent. of the cross-section of the column.

Just as the electric capacity of a plate is not considerably affected by cutting parts of it away and leaving an open framework, so also it is possible to block out a considerable portion of the cross-section of a diffusive column without materially altering the general static conditions on which the flow depends. In such a case, what I have termed the *diffusive efficiency* of the system is but little affected.

I have here a demonstration of this principle in these two columns of gel into which a dye has been diffusing for some time. In one case the column is entirely unobstructed, whereas in the other such a perforated septum as I have described has been inserted in the line of flow, thus cutting off about 90 per cent. of its effective area. You will notice that the efficiency of the column has not been sensibly reduced in the latter case.

In the accompanying illustration (Fig. 9), I have attempted to illustrate in diagrammatic form the manner in which the parallel lines of flux in a diffusive column are modified by the interposition of such a perforated septum. It will be noted that as the stream lines approach the apertures they become convergent and gradually assume parallelism again on the other side, since the lines of flux, like lines of force, cannot intersect each other.

On the other hand, there is an increased gradient of density in the immediate neighbourhood of the apertures, as evidenced by the zones of equi-density coming closer together in this region, and producing a more rapid flow through the septum.

That such a theoretical system conforms to the actual facts is shown by the succeeding illustration (Fig. 10), which shows a photograph of the zones of equi-density under these conditions produced

by intermittent diffusion of two reacting substances through a series of apertures.

In this principle resides the long-sought explanation of the effectiveness of the stomata of a green leaf in accelerating the interchanges of gases and water vapour which are requisite for the requirements of the plant.

From the dimensions and mode of distribution of these stomata, it is quite possible to calculate what their maximum diffusive efficiency ought to be under given conditions, both for carbon dioxide and water vapour, and to compare this with the actual interchanges as determined by experiment.

In all such cases as have been examined the theoretical efficiency of the mechanism, regarded merely as a piece of physical apparatus, is far in excess of any demands which could be made upon it. Whatever limiting factors may exist in the co-ordinated processes attendant on carbohydrate assimilation by a green leaf, whether of a physical or chemical nature, we cannot attribute any of them to faulty construction in the diffusive mechanism itself.

It is certainly extremely improbable that the green leaf is the only case in nature in which there has been a more or less perfect adaptation to these laws of diffusion through small apertures. It is true that up to the present it is the only instance in which a complete and satisfactory demonstration has been forthcoming of this remarkable adjustment of structure to function, but doubtless there exist many other examples of equal interest and importance which await further discovery. It is impossible, for instance, to observe the minute perforations in the closing membranes of certain vegetable cells without recognising how eminently suited these structures are for producing all the diffusive phenomena which belong to multi-perforate septa, and how admirably they are adapted, without any sacrifice of protective strength, to enhancing the rate of diffusive flow through the cell membrane separating contiguous cells.

Nor are these suggestive facts by any means confined to the Vegetable Kingdom.

It is many years ago since Graham hazarded the opinion that when insects are at rest and exerting no muscular effort of any kind, their respiratory processes are carried on entirely by diffusion along the ramifying tracheæ which communicate with the outer air through the stigmatic openings in the body segments.

The accuracy of this guess is rendered still more probable when we examine the structure of these stigmatic openings more closely.

I am indebted to Mrs. Cuthbert Baines for a beautiful microscopical drawing of the stigma of a caterpillar in medial cross-

section, from which you will see that the apparatus has in certain respects such a remarkable resemblance to the stoma of a leaf that it is impossible to avoid the conclusion that the gaseous exchanges of respiration in the insect are in a measure determined by this particular structure (see Fig. 11).

To elaborate and give the necessary proof of many of the statements I have made this evening would require, not one, but many lectures. The present summary, imperfect and discursive as it may appear, may nevertheless suffice to show that much may be expected from a continued study of diffusion and the application of its principles in various branches of science. One of the greatest pleasures of which the human mind is capable is engendered by this linking together of diverse sets of phenomena by some underlying common principle which is not at first recognisable. How well was this expressed nearly two thousand years ago by one who was both a great poet and a keen observer of nature—one who found his best solace and inspiration in the study of his forests, his flocks and herds, his vineyards, his corn lands and his hives!

"Felix qui potuit rerum cognoscere causas."

XLVI.—*Some Piperylhydrazones.*

By Albert Weinhagen.

The piperylhydrazine employed in this investigation was prepared by reducing nitrosopiperidine (Knorr, *Annalen*, 1883, **221**, 304). Unless otherwise stated, the condensations were effected according to the usual method of heating the aldehydes with the requisite amount of piperylhydrazine in alcoholic solution faintly acidified with acetic acid. As described in each instance, the products were then purified by such methods as proved most suitable.

Piperonalpiperylhydrazone.—This crystallises from alcohol in colourless needles melting at 65—67°. The hydrazone is readily soluble in ether, chloroform, benzene, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0·1916 gave 21·1 c.c. N_2 at 17° and 722 mm. N = 12·31.

$C_{13}H_{16}O_2N_2$ requires N = 12·07 per cent.

Salicylaldehydepiperylhydrazone.—This compound crystallises from alcohol in needles, at times in small rhombic plates, and

occasionally in octahedra, which interlace in such a manner as to form long, needle-like, prismatic structures. The compound melts at 71—72°, and is readily soluble in ether, chloroform, benzene, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0·1965 gave 24·7 c.c. N_2 at 17° and 711 mm. N=13·84.
$C_{12}H_{16}ON_2$ requires N=13·74 per cent.

Formaldehydepiperylhydrazone.—This crystallises from alcohol in prismatic needles melting at 78—79°. It is readily soluble in chloroform, hot light petroleum, or hot alcohol, less readily so in cold light petroleum or cold alcohol, and practically insoluble in water:

0·1270 gave 28·3 c.c. N_2 at 16° and 728 mm. N=25·21.
$C_6H_{12}N_2$ requires N=25·21 per cent.

Benzaldehydepiperylhydrazone.—This hydrazone crystallises from alcohol in small, five- or six-sided plates. The pure compound (which was analysed) melted at 68—69° (Knorr, *loc. cit.*, gives 62—63°, and Forster, T., 1915, **107**, 267, gives 68°).

Anisaldehydepiperylhydrazone.—Three grams of anisaldehyde were heated on the water-bath with 2 grams of piperylhydrazine and 2 grams of 50 per cent. acetic acid. The mixture soon became red, and ultimately an intensely reddish-violet syrup separated, which became crystalline on evaporating to dryness and allowing to remain for some time. By means of light petroleum, the hydrazone can be extracted from this mixture free from the red colouring matter, for the latter, whilst being readily soluble in alcohol, is quite insoluble in the former solvent. On evaporating the light petroleum, the hydrazone was obtained in small, colourless, hexagonal plates. The hydrazone obtained in this way possessed the property of turning reddish-violet when exposed to light, which was evidently due to traces of impurities. This ceased to be the case after it had been recrystallised from alcohol several times. The melting point ultimately remained constant at 54°. The hydrazone is readily soluble in ether, chloroform, light petroleum, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0·1897 gave 21·8 c.c. N_2 at 16° and 728 mm. N=12·79.
$C_{13}H_{18}ON_2$ requires N=12·85 per cent.

An attempt was made to avoid the formation of the reddish-violet colouring matter by condensing in alcoholic solution, but the results were precisely the same as before.

p-*Hydroxybenzaldehydepiperylhydrazone.* — This compound

separated from an alcoholic solution of 3 grams of piperylhydrazine, 4·5 grams of *p*-hydroxybenzaldehyde, and acetic acid, which had remained at the ordinary temperature for several days, whereas if the mixture is heated, a much inferior yield, accompanied by resinous red by-products, is obtained. The hydrazone is soluble in ether, chloroform, or hot alcohol. When recrystallised from the latter solvent, it melts at 161°:

0·1799 gave 22·7 c.c. N_2 at 18° and 726 mm. N=13·91.

$C_{12}H_{16}ON_2$ requires N=13·74 per cent.

p-*Aminoacetophenonepiperylhydrazone*.—Three grams of *p*-aminoacetophenone dissolved in alcohol were heated on the water-bath with 2 grams of piperylhydrazine and 2 grams of 50 per cent. acetic acid. The solution soon became yellow, and on cooling the mixture and allowing it to remain, no hydrazone separated. The mixture was accordingly evaporated to dryness. The brown, syrupy substance obtained in this way was practically insoluble in light petroleum, but treatment with this solvent converted it into a granular, faintly yellow mass, which was recrystallised from 95 per cent. alcohol several times. The pure white hydrazone obtained in this way crystallises in small prisms and prismatic needles melting at 108°. It is readily soluble in ether or hot alcohol, less readily so in cold alcohol, very sparingly so in light petroleum, and practically insoluble in water:

0·1468 gave 0·0110 H_2O at 110°. H_2O=7·49.

0·1889 ,, 30·4 c.c. N_2 at 16° and 728 mm. N=17·90.

$C_{13}H_{19}N_3,H_2O$ requires H_2O=7·66; N=17·89 per cent.

Hot dilute hydrochloric acid readily resolves this hydrazone into its components, of which *p*-aminoacetophenone was isolated and recognised by means of its platinichloride (Found: Pt=28·78. Calc.: Pt=28·69 per cent.).

Attempts to prepare the piperylhydrazones of propionaldehyde, acetone, *p*-aminobenzaldehyde, dextrose, galactose, and *l*-xylose gave rise to resinous red and brown products, whereas *iso*valeraldehyde furnished very small yields of a compound melting at approximately 122°, which was not analysed.

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[*Received, April* 17*th*, 1918.]

XLVII.—*Acetyl-*p*-diazoimides derived from Substituted* p*-Phenylenediamines.*

By Gilbert T. Morgan and David Alexander Cleage.

Recent experiments on the diazotisation of acyl-*p*-phenylenediamines carried out with nitrous anhydride in dry solvents have led to the isolation of the simpler acyl-*p*-phenylenediazoimides containing respectively formyl, acetyl, and benzoyl groups (Upton and Morgan, T., 1917, **111**, 187). These results have since been confirmed by Dimroth and Leichtlin (*Ber.*, 1917, **50**, 1539), who have prepared benzoyl-*p*-phenylenediazoimide in aqueous solutions by the action of sodium hydroxide on benzoylaminonaphthalene-4-diazonium chloride.

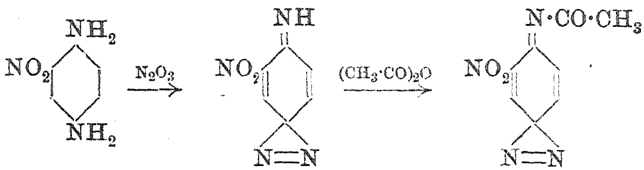
Researches extending over many years have shown that the formation of acyl-*p*-diazoimides from aromatic acyl-*p*-diamines is a general reaction which has been realised in a very large number of instances (T., 1905, **87**, 73, 921, 1302; 1906, **89**, 4, 1158, 1289; 1907, **91**, 1505, 1512; 1908, **93**, 602, 614; 1910, **97**, 48; *Ber.*, 1902, **35**, 888; 1906, **39**, 2869).

These results indicate that the presence of the acyl group doubtless plays an important part in the internal condensation leading to the production of acyl-*p*-diazoimides, yet there is a possibility that under suitable experimental conditions it might be possible to isolate the parent substances of this series of diazo-derivatives in which the acyl radicle is replaced by hydrogen.

With this object in view, the experiments recorded in the experimental section have been made on derivatives of *p*-phenylenediamine containing acidic substituents in the nucleus.

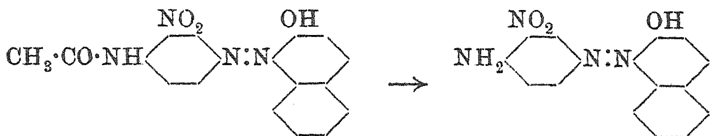
The difficulty of diazotising both amino-groups simultaneously in *p*-phenylenediamine is greatly increased when a nitro-group is introduced into the ring. Nitro-*p*-phenylenediamine (I) is accordingly a suitable base for the attempt to isolate a diazoimine produced by the diazotisation of only one of the amino-groups.

When this experiment is carried out with nitrous anhydride in well-cooled anhydrous solvents, an unstable, brown substance having the properties of a diazoimine (II) is produced. This product, however, becomes resinous when warmed to the ordinary temperature; it is stable only in a freezing mixture. While suspended in a cooled mixture of ether and acetone, this diazoimine can, however, be stabilised by acetylation with acetic anhydride, when *4-acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide* (III) is obtained:



(I.) (II.) (III.)

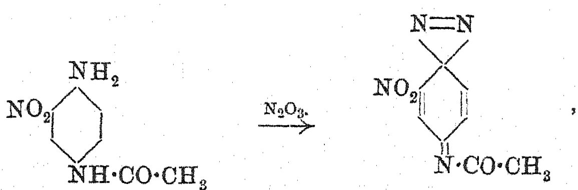
The constitution of this acetyl derivative, and hence that of the unstable diazoimine, are confirmed by the following series of reactions. The acyl-*p*-diazoimide is combined with β-naphthol to form the azo-derivative (IV), and this compound is hydrolysed to the



(IV.) (V.)

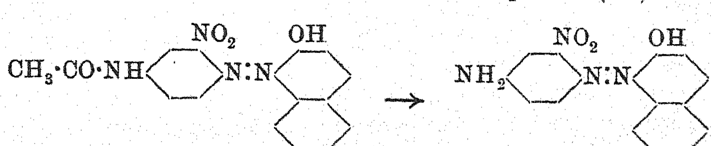
corresponding aminoazo-derivative (V). The latter product when diazotised and boiled with alcohol is converted into *m*-nitrobenzene-azo-β-naphthol, which is identified by direct comparison with the preparation obtained by combining diazotised *m*-nitroaniline and β-naphthol.

Further confirmation of this constitution for 4-acetyl-3-nitrophenylene-1-diazo-4-imide is obtained by preparing its isomeride, 4-*acetyl*-2-*nitro*-p-*phenylene*-1-*diazo*-4-*imide* (VII). This diazoimide, obtained in a similar manner by diazotising 4-acetyl-2-nitro-*p*-phenylenediamine (VI) with nitrous anhydride in dry acetone,



(VI.) (VII.)

combines with β-naphthol to yield an azo-derivative (VIII), which on hydrolysis gives rise to an aminoazo-compound (IX). From

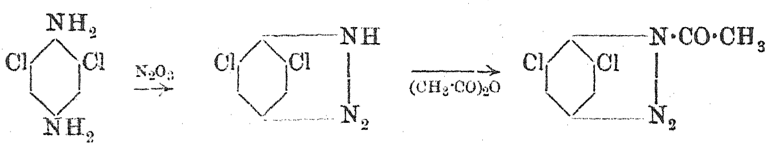


(VIII.) (IX.)

this aminoazo-derivative, elimination of the amino-group through the diazo-reaction leads to *o*-nitrobenzeneazo-β-naphthol, which can be compared directly with the product obtained by combining *o*-nitrobenzenediazonium chloride and β-naphthol.

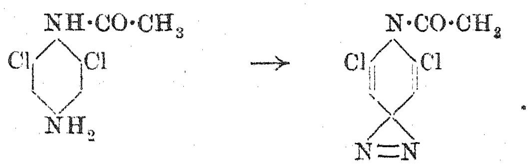
These results demonstrate the constitution of the two isomeric acetyl-*p*-diazoimides (III and VII) derived from 2-nitro-4-phenylenediamine, the former of which is obtained by acetylating the diazoimine of this diamine.

Similar results have been obtained in the case of 2:6-dichloro-4-phenylenediamine. This base on treatment with nitrous anhydride in well-cooled acetone yields an unstable diazoimine which can be stabilised by acetylation:



(X.)

The product (X), a grey, crystalline powder, combined readily with the naphthols and naphthylamines, giving colour reactions identical with those obtained from the diazoimide (XI) prepared by diazotising 1-acetyl-2:6-dichloro-*p*-phenylenediamine:

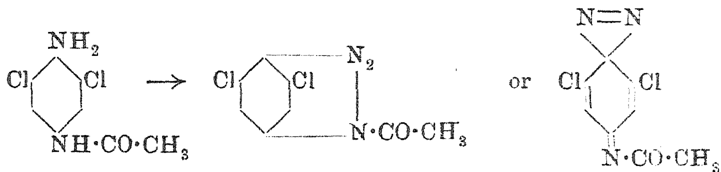


(XI.)

The latter diazoimide has, however, a bright yellow colour. The colour differences may possibly be due to the first compound being the cyclic diazoimide (X), whilst the latter is the diazoquinone-imide (XI). Or, alternatively, the less coloured compound might be a diazonium derivative and the other a diazo-compound. These differences, however, disappear on combining with phenols or reactive bases both forms of *acetyl*-3:5-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide* giving the same azo-derivatives.

The alternative formulations (XII or XII*a*) for the product of acetylation of 2:6-dichloro-*p*-phenylenediamine is excluded by direct experimental evidence.

Acetyl-2:6-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide* (XII) is prepared by treating 4-acetyl-2:6-dichloro-*p*-phenylenediamine with nitrous anhydride under similar conditions:



(XII.) (XIIa.)

The product, which is stable at the ordinary temperature, is almost colourless, thus suggesting the diazoimide configuration (XII) rather than that of the diazoquinoneimide (XII*a*). It combines readily with the naphthols and naphthylamines, giving colour indications differing from those of the two forms of acetyl-3:5-dichloro-*p*-phenylene-1-diazo-4-imide.

EXPERIMENTAL.

4-*Acetyl-2-nitro*-p-*phenylene*-1-*diazo*-4-*imide* (VII).

p-Phenylenediamine was acetylated by adding acetic anhydride (1·3 parts) to its 40 per cent. aqueous solution. The diacetyl derivative when nitrated either in glacial acetic acid or in concentrated sulphuric acid (compare *Ber.*, 1897, **30**, 980) gave its own weight of diacetyl-2-nitro-*p*-phenylenediamine. This product was half hydrolysed to 4-acetyl-2-nitro-*p*-phenylenediamine by boiling for fifteen minutes with 2 parts of crystallised barium hydroxide and 3 parts of water, the barium being then removed by passing carbon dioxide into the boiling solution. The filtrate on cooling deposited bulky, orange-red plates melting at 188°.

4-Acetyl-2-nitro-*p*-phenylenediamine (1 part) dissolved in 100 parts of pure dehydrated acetone was treated slowly with 5 c.c. of a 10 per cent. acetone solution of nitrous anhydride free from nitrogen peroxide, both solutions being cooled to −15°. The colour of the solution of the base changed from red to pale straw-yellow, and on the addition of an equal volume of pure dry ether the product separated in yellow plates, and was washed with anhydrous ether and dried in a vacuum desiccator in the dark:

0·1000 gave 22·5 c.c. N_2 (moist) at 9° and 770·8 mm. N = 27·31.
$C_8H_6O_3N_4$ requires N = 27·18 per cent.

4-*Acetyl-2-nitro*-p-*phenylene*-1-*diazo*-4-*imide* decomposed explosively at 142°. It darkened on exposure to light, and combined readily with β-naphthol when the two reagents were ground together.

Constitution of Acetyl-2-nitro-p-phenylene-1-diazo-4-imide.

Acetyl-2-nitrophenylene-1-diazo-4-imide was combined with β-naphthol (1 mol.) in glacial acetic acid. The product, a red azo-β-naphthol, melted at 298°, and developed a magenta coloration with concentrated sulphuric acid. When the saturated solution of this azo-derivative in glacial acetic acid was diluted with three volumes of water and warmed with excess of concentrated ammonia, the acetyl group was removed by hydrolysis. The resulting 2-nitro-4-aminobenzeneazo-β-naphthol was dissolved in absolute alcohol and treated with nitrous anhydride and a few drops of concentrated sulphuric acid at −10° to −15°. This diazonium solution combined with alkaline β-naphthol to a dark red bisazo-compound, giving an orange coloration with concentrated sulphuric acid. Another portion of the alcoholic diazonium solution was boiled gently, when nitrogen was evolved. The dark red powder left on evaporating the alcoholic solution was crystallised from 80 per cent. alcohol containing animal charcoal. It then melted at 206° and gave a reddish-violet coloration with concentrated sulphuric acid. A specimen of 2-nitrobenzeneazo-β-naphthol was prepared for comparison from β-naphthol and diazotised *o*-nitroaniline; it was a brownish-red to dark red powder melting at 209° and giving a violet coloration with concentrated sulphuric acid. The melting point of a mixture of the two preparations varied from 203° to 205°. In this way, the orientation of the nitro-group with respect to the diazo-group was ascertained and the constitution of the acetyl-diazoimide determined. *4-Acetyl-2-nitro-p-phenylene-1-diazo-4-imide* gave the following colour reactions on conversion into its azo-derivatives, this combination being effected in pyridine:

Azo-derivative with:	Colour of the azo-derivatives.	Coloration with concentrated sulphuric acid.
β-Naphthol	Scarlet	Magenta
β-Naphthylamine	Red	Brownish-red
α-Naphthol	Scarlet	Emerald green
α-Naphthylamine	Crimson	Purple

3-Nitro-p-phenylene-1-diazo-4-imine and its Acetyl Derivative.

2-Nitro-*p*-phenylenediamine in dry acetone solution yielded on treatment with nitrous anhydride dissolved in the same solvent a diazo-derivative which separated as a brown, crystalline precipitate on adding dry ether at −15°. On attaining the ordinary temperature, this product resinified and lost its power of combining with β-naphthol to form an azo-derivative.

The acetyl derivative of this unstable diazo-compound was isolated by the following procedure. 4-Acetyl-2-nitro-*p*-phenylenediamine (1 gram) dissolved in 100 c.c. of dry acetone was treated successively with 10 c.c. of a 10 per cent. acetone solution of nitrous anhydride and 0·40 c.c. of acetic anhydride. The colour of the solution of the base changed from crimson to brown. The addition of 80 c.c. of ether produced a precipitate, probably consisting of unacetylated diazoimine, which dissolved again as acetylation proceeded, the acetyl derivative separating on the addition of a further 100 c.c. of ether in brownish-red plates exploding violently at 140°:

0·1500 gave 35·3 c.c. N_2 at 18° and 773·6 mm.* N = 27·70.
$C_8H_6O_3N_4$ requires N = 27·18 per cent.

*Constitution of 4-Acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide.*

The azo-β-naphthol compound of 4-acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide was a dark red powder melting above 290°. Its saturated solution in glacial acetic acid was diluted with three volumes of water and the liquid rendered alkaline with concentrated aqueous ammonia. This treatment led to hydrolysis of the acetyl group in the azo-derivative. The resulting 3-nitro-4-aminobenzeneazo-β-naphthol, a pale brown powder melting at 208°, and developing a claret coloration with concentrated sulphuric acid, was diazotised by adding nitrous acid at −10° to −15° to its solution in absolute alcohol. The diazo-compound gave with alkaline β-naphthol a brown bisazo-derivative, developing a yellow coloration with concentrated sulphuric acid.

On warming an alcoholic solution of the diazo-compound of 3-nitro-4-aminobenzeneazo-β-naphthol, nitrogen was evolved, and the liquid on evaporation left a dark, tarry mass from which 3-nitrobenzeneazo-β-naphthol was extracted on boiling with 80 per cent. alcohol and animal charcoal. The filtrate on cooling deposited bright yellowish-orange crystals which melted at 192°, and developed a bright cherry-red coloration with concentrated sulphuric acid. For the purpose of comparison, *m*-nitroaniline was converted successively into 3-nitrobenzenediazonium chloride and 3-nitrobenzeneazo-β-naphthol. The latter compound melted at 194° and gave a similar cherry-red coloration with concentrated sulphuric acid. The melting point of a mixture of the two preparations varied between 189° and 192°.

*4-Acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide* gave the following

* In this and the following estimations the nitrogen was measured over 50 per cent. potassium hydroxide

colour reactions when converted into its azo-derivatives by combining in the presence of pyridine:

Azo-compound with:	Colour of azo-compound.	Coloration with concentrated sulphuric acid.
β-Naphthol	Brownish-red	Magenta red
β-Naphthylamine	Brownish-red	Brown
α-Naphthol	Reddish-brown	Olive green
α-Naphthylamine	Dark red	Magenta red

*Acetyl-*p*-diazoimides derived from* 2:6-*Dichloro-*p*-phenylenediamine.*

A solution of 1 part of *p*-nitroaniline in 3 parts of glacial acetic acid and 6 parts of concentrated hydrochloric acid was cooled to 0° and treated with chlorine until 2 molecular proportions of the gas had been used. The mixture was kept thoroughly stirred throughout the chlorination, and the lemon-yellow precipitate of 2:6-dichloro-4-nitroaniline was obtained in theoretical yield (compare Flürscheim, T., 1908, **93**, 1773). This nitro-compound (1 part) and ammonium chloride ($\frac{3}{8}$ part) were dissolved in 25 parts of 50 per cent. alcohol, and 1 part of zinc dust (80 per cent. Zn) was added slowly to the boiling solution. The mixture was heated under reflux for half an hour until the colour changed from yellow to light grey. The filtrate from the precipitate of zinc and zinc hydroxide was then distilled and the greater part of the alcohol thus recovered. 2:6-Dichloro-4-phenylenediamine separated from the residual solution in colourless plates, becoming brown with a bronzy reflex on exposure to the air. The yield was 90 per cent. of the calculated quantity.

*4-Acetyl-2:6-dichloro-*p*-phenylene-1-diazo-4-imide.*

2:6-Dichloro-*p*-phenylenediamine (1 part) dissolved in 50 parts of warm water was acetylated by the addition of 1 part of acetic anhydride. The solution, which was vigorously stirred during this reaction, became speedily filled with colourless crystals of 4-acetyl-2:6-dichloro-*p*-phenylenediamine. The crude product was then recrystallised from hot water, from which it separated in colourless needles melting at 200°. One part of this acetyl compound dissolved in 100 parts of dry acetone and cooled to −15° was diazotised with 8·5 parts of a 10 per cent. solution of nitrous anhydride in the same solvent. On adding 100 parts of dry ether, the diazoimide separated as a pale yellowish-white, microcrystalline precipitate:

0·1500 gave 23·2 c.c. N_2 at 18·5° and 773 mm. N=18·27.

$C_8H_5ON_3Cl_2$ requires N=18·25 per cent.

*4-Acetyl-2 : 6-dichloro-*p*-phenylene-1-diazo-4-imide* was obtained in almost colourless plates decomposing explosively at 138°. This diazoimide coupled additively with the following developers either in the dry state or when mixed with pyridine:

Developer.	Colour of Azo-compound.	Coloration with concentrated sulphuric acid.
β-Naphthol	Orange-red	Bluish-red
β-Naphthylamine	Brownish-red	Brown
α-Naphthol	Brownish-red	Green
α-Naphthylamine	Red	Reddish-brown
Chromotropic acid...........	Cerise	Olive green

*1-Acetyl-3 : 5-dichloro-*p*-phenylene-1-diazo-4-imide.*

(1) *Preparation from 1-Acetyl-2 : 6-dichloro-*p*-phenylenediamine.*—2 : 6-Dichloro-4-phenylenediamine (10 grams) was heated for one hour in a reflux apparatus with 10 c.c. of acetyl chloride, when diacetyl-2 : 6-dichloro-*p*-phenylenediamine separated on cooling. The crude product when crystallised from hot water melted at 254°. 1-Acetyl-2 : 6-dichloro-*p*-phenylenediamine was prepared by half hydrolysing the diacetyl compound. The latter was boiled for fifteen minutes with 30 parts of *N*-sodium hydroxide solution, when, on cooling, the monoacetyl derivative separated in lustrous, colourless plates which, after recrystallisation from water, melted at 218°. Three parts of 1-acetyl-2 : 6-dichloro-*p*-phenylenediamine dissolved in 120 parts of dry acetone were diazotised with 1 part of nitrous anhydride dissolved in 10 parts of the same solvent. During diazotisation, the solution was thoroughly stirred, when the colour changed to bright yellow; the precipitation of yellow diazoimide then commenced, and was completed by the addition of 60 parts of dry ether:

0·2050 gave 32·5 c.c. N_2 at 18° and 762 mm. N=18·37.

$C_8H_5ON_3Cl_2$ requires N=18·25 per cent.

*1-Acetyl-3 : 5-dichloro-*p*-phenylene-1-diazo-4-imide* is an orange-yellow, crystalline powder, very sensitive to light, changing rapidly to chocolate, and decomposing at 133°. It combined additively with the following developers on mixing either in the dry state or in pyridine:

Developer.	Colour of azo-compound.	Coloration with concentrated sulphuric acid.
β-Naphthol	Orange-red	Scarlet
β-Naphthylamine	Orange	Blue
α-Naphthol	Brownish-red	Green
α-Naphthylamine	Orange	Scarlet

(2) *Preparation from 2 : 6-Dichloro-*p*-phenylenediamine.*—2 : 6-Dichloro-*p*-phenylenediamine (1 part) dissolved in 40 parts of dry

acetone at $-10°$ was diazotised with 0·85 part of nitrous anhydride in a 10 per cent. acetone solution. The solution, which was stirred mechanically, became slightly paler in colour, and on the addition of 2 parts of acetic anhydride gave a dark grey, flocculent precipitate. This substance, which decomposed explosively at 138°, was very sensitive to light and darkened on exposure:

0·2000 gave 33·25 c.c. N_2 at 19° and 759 mm. N=19·11.

$C_8H_5ON_3Cl$ requires N=18·25 per cent.

This specimen of diazoimide, combined in pyridine with the following developers, gave the same colour reactions as those obtained in the foregoing preparation:

Developer.	Colour of azo-derivative.	Coloration with concentrated sulphuric acid.
β-Naphthol	Orange-red	Scarlet
β-Naphthylamine	Orange	Blue
α-Naphthol	Brownish-red	Green
α-Naphthylamine	Orange	Scarlet

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[*Received, June 20th*, 1918.]

XLVIII.—*A New Form of Methylgalactoside and its Conversion into Octamethyldigalactose and into a Methyldigalactoside.*

By Mary Cunningham.

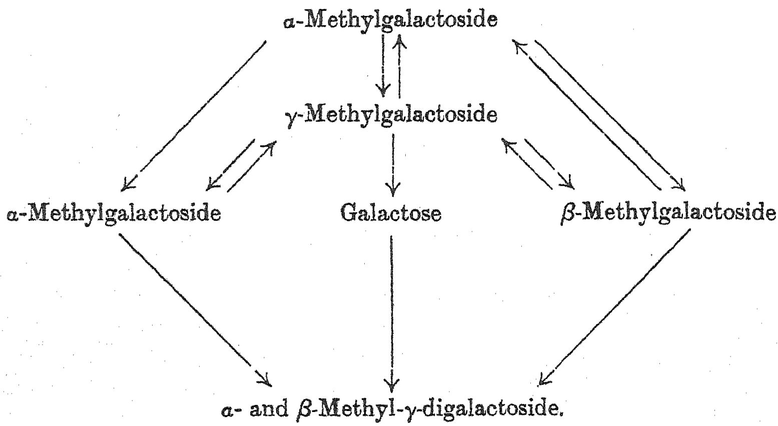
The isolation of a new form of methylglucoside by Fischer (*Ber.*, 1914, **47**, 1980), and the detailed study of its derivatives by Irvine, Fyfe, and Hogg (T., 1915, **107**, 524), naturally suggests the possibility that members of the dulcitol series of hexoses may also exhibit the same structural isomerism. Observations have, in fact, already been recorded indicating that galactose can react in a form other than the α- and β-modifications, and recently all doubt on this point has been removed by the preparation of four galactose pentaacetates by Hudson and his co-workers (*J. Amer. Chem. Soc.*, 1916, **38**, 1223). The first mention of this unexpected isomerism occurs, however, in Fischer's original description of the methylhexosides (*Ber.*, 1895, **28**, 1174). By concentrating an acid methyl-alcoholic solution of the crystalline α- and β-methylgalactosides, an amorphous product was obtained which Fischer regarded as a third form of methylgalactoside. The absence of analytical data

rendered complete identification of this substance impossible, and some years later Irvine and Cameron (T., 1905, 86, 907) suggested that a methylated galactoside prepared by them and found to possess abnormal properties might be a derivative of the third isomeride referred to by Fischer. In this research, Irvine and Cameron isolated a syrupy form of methylgalactoside, which from its low specific rotation was at first regarded as consisting mainly of the β-modification. This particular methylhexoside is now shown to be a true methylgalactoside of the γ-series resembling γ-methylglucoside in its properties, but it is not identical with Fischer's amorphous product, which, as shown by analysis and a molecular weight determination, is a *methyldigalactoside*. The new form of methylgalactoside gives on methylation, followed by hydrolysis, tetramethyl γ-galactose, identical with the compound previously prepared by Irvine and Cameron (*loc. cit.*), and this sugar has now been found to possess the unique property of undergoing auto-condensation to give octamethyl γ-digalactose. The reaction in question proceeds spontaneously at the ordinary temperature and in the absence of any recognisable catalyst. This is, of course, a most unusual result, and, taken in conjunction with the formation, in somewhat similar circumstances, of a substituted disaccharide derivative from γ-methylglucoside (Irvine, Fyfe, and Hogg, *loc. cit.*), it serves to emphasise the extraordinarily reactive character of ethylene–oxide sugars. Moreover, it has been shown that the reaction which gives rise to methyldigalactoside also involves the presence—probably only transitory—of a variety of galactose conforming to this particular type of sugar. This conclusion seems warranted by the fact that the digalactoside, as shown by a study of its behaviour on hydrolysis, consists of the stable forms of methylgalactoside (α- and β-) united to the unstable form of the sugar. The union involves the reducing group of the latter, and accordingly the structure of the complex is represented by the formula

$$\mathrm{MeO{\cdot}\underbrace{CH{\cdot}[CH{\cdot}OH]_2{\cdot}CH}_{O}{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}\underbrace{CH{\cdot}CH}_{O}{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH.}$$

A significant observation is that no structural modification of the digalactoside can be obtained by varying the form of methylgalactoside employed in its preparation. Thus, whether the starting point is an acid, methyl-alcoholic solution of pure α-, pure γ-, or an equilibrium mixture of α- and β-methyl-galactosides, a compound having the same constants and properties and giving the same results on hydrolysis is formed in each case. The most prob-

able explanation of this rather surprising result seems to be that under the influence of acid methyl alcohol, any one form of methylgalactoside passes to an equilibrium mixture of the three isomerides α-, β-, γ-, and of these the unstable γ-variety is subsequently hydrolysed on concentration to give the reactive type of the sugar. This immediately combines with the stable hexosides to give a non-reducing complex, regeneration of γ-methylgalactoside being impossible owing to the removal of the alcohol. The course of the reaction would be represented by the following scheme:



These suggestions are, moreover, in accord with the results previously obtained by Irvine and Cameron (T., 1905, **86**, 907), who found that fully methylated hexosides of stable form could be heated at 110° to 150° without any hydrolysis occurring, the only change observed being an interconversion to an equilibrium mixture of the α- and β-isomerides. In these experiments, the formation of the γ-variety was impossible owing to the presence of the methoxyl groups, so that the complicated reactions described above could not take place.

Experimental.

γ-Methylgalactoside.—Galactose was heated at 100° with methyl alcohol containing 0·25 per cent. of hydrogen chloride in essentially the way described by Fischer for the preparation of α- and β-methylgalactosides, except that the acid was neutralised before removing the solvent. The neutralised solution deposited crystals of α-methylgalactoside on slight concentration, and from the filtrate a viscid syrup was obtained on further heating. On the addition of ether, this syrup formed a semi-solid mass consisting for the

most part of α- and β-methylgalactosides, but on triturating the mass with small quantities of absolute alcohol, some of the adhering syrup passed into solution and was removed by filtration. In this manner, a nearly colourless syrup of a non-reducing character was prepared which, in order to remove impurities, was dissolved in methyl alcohol and the solution fractionally precipitated by successive additions of ethyl acetate. The yield was 30 per cent. of the sugar used. For analysis, the syrup was dried to constant weight at 60°/20 mm. This method of preparation, it will be observed, differs considerably from that described by Fischer (*loc. cit.*) for the isolation of γ-methylglucoside, and it seems to point to the interesting conclusion that in the ordinary process of hexoside synthesis, the three modifications, α-, β-, and γ-, are produced together.

Found: C=42·94; H=7·3; OMe=15·7.

$C_7H_{14}O_6$ requires C=43·27; H=7·27; OMe=15·98 per cent.

The new compound thus isolated as a mixture of stereoisomerides showed the characteristic reactions of derivatives of the γ-series and gave $[\alpha]_D$ +12·95° in methyl alcohol and +25·9° in water. It should be mentioned that attempts to prepare acetone derivatives similar to γ-methylglucosidemonoacetone were entirely unsuccessful.

Hydrolysis of γ-Methylgalactoside.—γ-Methylgalactoside is somewhat more stable towards dilute acids than the corresponding glucoside, as it is necessary to carry out the hydrolysis with N/100-hydrochloric acid at 100°. The changes in optical activity observed are shown in Fig. 1, and it will be seen that the specific rotation increases without any irregularities until the value for galactose is reached, at the end of four and a-half hours. The continuity of the curve might at first suggest that only one of the two possible modifications of the ethylene–oxide type was present, but subsequent methylation showed the existence of the two varieties. The form of the curve does, however, prove that Fischer's amorphous product cannot be one of these γ-isomerides. This compound is more dextrorotatory than galactose itself, and if it were present, the curve would show a point above the specific rotation of galactose before the constant value was reached.

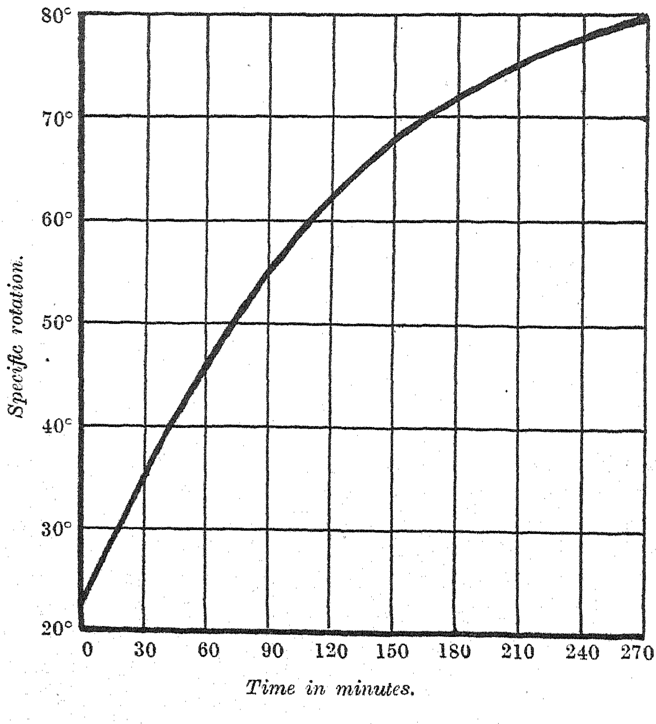
Tetramethyl γ-Methylgalactoside.—γ-Methylgalactoside was methylated by the silver oxide method under the usual conditions, and the alkylation proceeded normally. After three methylations, the product was extracted with ether, and on distilling at 142—145°/12 mm., a colourless, mobile liquid was obtained having $[\alpha]_D$ +3·98° in alcohol. The value given by Irvine and Cameron for their abnormal form of tetramethyl methylgalactoside was

$+4{\cdot}06°$, so that the two compounds are identical. Fractionation separated the distillate into two portions; the one boiling at 135°/12 mm. gave $[\alpha]_D$ $-4{\cdot}3°$, and the other, boiling at 150°/12 mm., showed $[\alpha]_D$ $+8{\cdot}8°$, but the analytical composition of each fraction was identical.

Hydrolysis of Tetramethyl γ-Methylgalactoside, Tetramethyl γ-Galactose, and Octamethyl γ-Digalactose.—The methylated galactoside is only completely converted into the corresponding

FIG. 1.

Hydrolysis of γ-methylgalactoside.

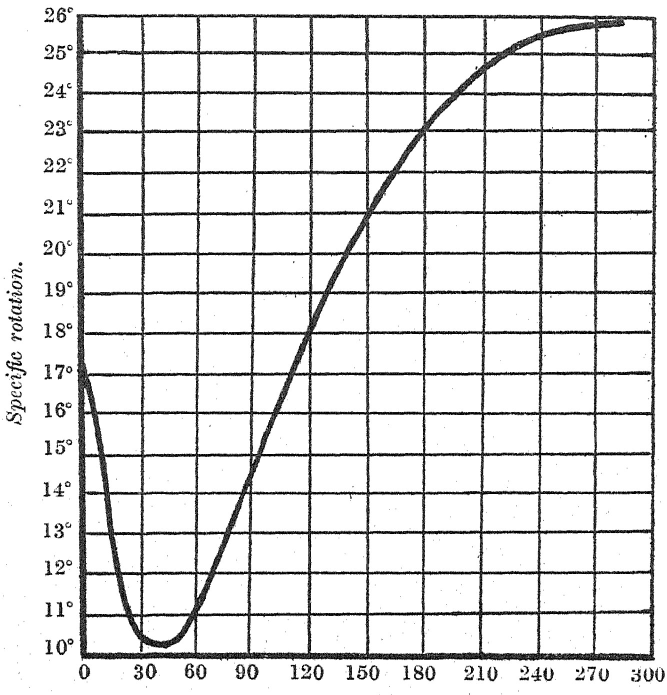


sugar by heating at 100° with $N/100$-hydrochloric acid for eight hours, and consequently hydrolysis experiments were carried out with $N/10$-acid at 100°. As shown on the accompanying curve (Fig. 2), the specific rotation falls initially and then rises, the constant value $+25{\cdot}9°$ being reached at the end of five hours. The specific rotation given by Irvine and Cameron (*loc. cit.*) for the methylated sugar was $26{\cdot}1°$, so that there was no doubt that tetramethyl γ-galactose was present, but as new and unexpected cases

of auto-condensation had recently been observed, the sugar, isolated as usual, was left to remain for some time before distillation with the idea that a disaccharide derivative might possibly be formed. After an interval of seven days, the syrup was distilled at the low pressure of the Gaede pump. The distillate (b. p. 114—117°/0·03 mm.), which was a colourless syrup, had now lost the properties of a reducing sugar and acquired those of a glucoside. More-

FIG. 2.

Hydrolysis of tetramethyl γ-methylgalactoside.



over, the specific rotation had increased greatly, the values for $[\alpha]_D$ in alcohol and water being +54·4° and +75° respectively. As was to be expected, the new compound reduced potassium permanganate solution instantaneously.

Found: C=52·2, 52·4; H=8·5, 8·7; OMe=57·1, 57·3.

$C_{20}H_{38}O_{11}$ requires C=52·86; H=8·4; OMe=54·6 per cent.

The analytical figures indicate that the compound is octamethyldigalactose; but it is obviously not quite pure.

Hydrolysis of Octamethyl γ-Digalactose.—On heating a solution of the methylated disaccharide in $N/10$-hydrochloric acid at 100°, the specific rotation decreased, and at the end of eight and a-half hours reached the constant value $+25 \cdot 6°$, which agrees with the figure previously found for tetramethyl γ-galactose, and establishes the compound as essentially a disaccharide derivative.

Methyldigalactoside (1) *from α- and β-Methylgalactosides.*—A solution of 10 grams of an equilibrium mixture of α- and β-methylgalactosides in 50 c.c. of methyl alcohol was concentrated to a viscid syrup, which was dissolved in methyl alcohol and the solution filtered. Addition of absolute alcohol to the filtrate gave a white, amorphous product of an extremely deliquescent nature which, after remaining for some time in a vacuum, was dried to constant weight at 70°/20 mm. The compound behaved as a glucoside to Fehling's solution, and gave $[\alpha]_D$ in methyl alcohol $+85 \cdot 6°$ and in water $+101 \cdot 1°$.

Found: C=43·88; H=6·9; OMe=9·05.
$C_{13}H_{24}O_{11}$ requires C=43·8; H=6·8; OMe=8·7 per cent.

A molecular weight determination by the cryoscopic method gave M.W.=341; $C_{13}H_{24}O_{11}$ requires M.W.=356.

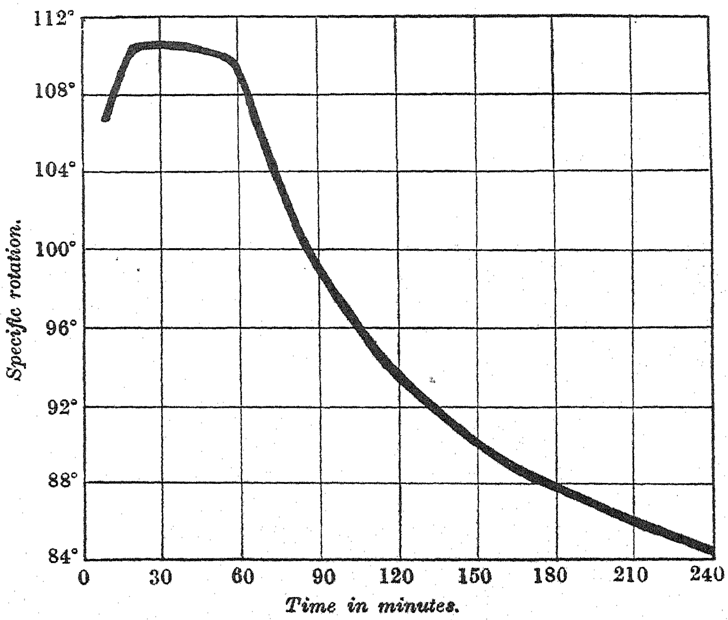
An estimation by the ebullioscopic method could not be carried out, owing to the sparing solubility of the compound in any suitable solvent.

Hydrolysis of Methyldigalactoside.—The digalactoside showed the marked instability towards neutral potassium permanganate solution characteristic of ethylene–oxide compounds, so that it evidently contained one or more unstable linkings, and as these are ruptured by heating at 100° with $N/100$-hydrochloric acid, their number and position in the molecule of the digalactoside could be ascertained by following the course of the hydrolysis with the polarimeter. The specific rotation was found to increase and reached a constant value at the end of three hours, whilst the solution acquired reducing properties. This reduction was entirely due to the formation of galactose, as indicated by the fact that treatment with phenylhydrazine yielded galactosephenylosazone alone. At the same time, a methoxyl estimation carried out on the products isolated at this first stage of the hydrolysis showed that a hexoside was present. Hence the increase in specific rotation is not due to the formation of a disaccharide, but is occasioned by the liberation of α-methylgalactoside, $[\alpha]_D +180°$. The molecule of the digalactoside therefore contains only one unstable linking, which is situated in one of the sugar residues, and the stability of the glucosidic methyl group shows that this portion of the molecule

retains the normal butylene-oxide structure. These observations are summarised in the constitutional formula given on p. 597 The maximum value for the optical activity is, however, less than that required for an equimolecular mixture of α-methylgalactoside, $[\alpha]_D + 180°$, and galactoside, $[\alpha]_D + 81°$. This deficiency is most likely due to the presence of the practically inactive β-methylgalactoside, and the form of the rotation curve when the hydrolysis is carried out with $N/10$-hydrochloric acid supports this contention. The changes in specific rotation are shown in Fig. 3, and it will be

FIG. 3.

Hydrolysis of methyldigalactoside.



observed that the rapid rise to the maximum value in the first twenty minutes is succeeded by a constant period of forty minutes, during which the decline in activity due to the hydrolysis of the α-isomeride is balanced by the increase in activity occasioned by the more quickly hydrolysed β-form, whilst the marked fall in the next ten minutes indicates that this masking effect has now disappeared. The specific rotation then decreases regularly until the value for galactose is reached after four hours. This preparation of the digalactoside therefore undoubtedly consists of α- and β-methylgalactosides in union with γ-galactose.

Methyldigalactoside (2) *from γ-Methylgalactoside.*—γ-Methylgalactoside was treated in the same way as the mixture of α- and β-methylgalactosides. The compound isolated gave the same values for the specific rotation as the previous preparation, $+85{\cdot}6°$ in methyl alcohol and $101{\cdot}1°$ in water. On hydrolysis with $N/100$-hydrochloric acid at 100°, the specific rotation increased to the constant value $+109{\cdot}6°$ at the end of three hours, and after the acid concentration had been raised to $N/10$, the same characteristic points were observed as before. The specific rotation remained constant for forty minutes, and then fell sharply to $104{\cdot}5°$ in the next twenty minutes, after which it decreased steadily until the hydrolysis was complete.

Methyldigalactoside (3) *from α-Methylgalactoside.*—In this experiment, a specimen of α-methylgalactoside was used which had been several times recrystallised until entirely free from traces of either the β- or the γ-isomeride. The specific rotation of the digalactoside obtained was $+100{\cdot}9°$ in water, and this increased on heating with $N/100$-hydrochloric acid at 100° to the maximum value $110{\cdot}3°$ at the end of three hours. Thereafter the concentration of acid was changed as before, when the variations in activity previously described were again observed. The preparations of the digalactosides are therefore indistinguishable from each other.

I wish to express my indebtedness to Professor Irvine for valuable advice in carrying out this work.

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[*Received, April 23rd*, 1918.]

XLIX.—*The Application of the Auto-condensation Powers of γ-Sugars to the Synthesis of Carbohydrate Complexes.*

By MARY CUNNINGHAM.

THE preparation of γ-methylglucosidemonoacetone (Macdonald, T., 1913, **103**, 1896; Irvine, Fyfe, and Hogg, T., 1915, **107**, 524) and a comparison of the conditions under which the stable and unstable hexosides are formed suggest that the initial action of acid methyl alcohol on a reducing sugar may consist in transform-

ing a portion of it from the normal to the reactive form. This form of the sugar seems incapable of existence in the free state, and hence it would immediately combine with the alcohol to form a γ-methylhexoside. In the preceding communication it has been shown that if a solution of any one of the three isomeric methylgalactosides in acid methyl alcohol is concentrated, then a mixture of stereoisomeric condensation compounds results consisting of the stable hexosides united to γ-galactose. It seemed, therefore, not impossible that similar compounds might be formed by merely dissolving a reducing sugar in this reagent and concentrating the solution. The course of the anticipated reaction is represented by the following scheme:

$$
\begin{tikzcd}
\alpha\text{- and }\beta\text{-Hexose} \arrow[r] & \gamma\text{-hexose} \arrow[r] & \gamma\text{-methylhexosides} \arrow[dl] \arrow[dr] & \\
& \alpha\text{- and }\beta\text{-Methylhexosides} \arrow[dr] & & \gamma\text{-Hexose} \arrow[dl] \\
& & \text{Condensation compound.} &
\end{tikzcd}
$$

It was, of course, recognised that as the reaction could not be readily controlled, the γ-sugar formed might condense either with the stable hexosides or with a preformed complex, thus giving rise to products of greater complexity than the methyldigalactoside referred to, or even to mixtures of different complexes. These ideas were realised in that compounds containing two or more sugar molecules were obtained, galactose and dextrose giving respectively a methyltetragalactoside and a methyltetraglucoside, $C_{25}H_{44}O_{21}$, whilst maltose yielded a methyltrimaltoside,

$$C_{37}H_{64}O_{31},H_2O.$$

Compounds of a similar nature could not be prepared from fructose, as charring invariably occurred on concentrating a solution of the sugar in acid methyl alcohol, and, among the reducing disaccharides, lactose remained entirely unaffected by the reagent. The products behaved as glucosides towards Fehling's solution and showed the characteristic reactions of γ-compounds, whilst the results obtained on hydrolysis indicate that they are constituted similarly to methyldigalactoside, the glucosidic methyl group being attached to a sugar residue retaining the normal butylene–oxide structure, whilst the remaining sugar residues conform to the ethylene–oxide type. It should be mentioned that estimations of methoxyl have been chiefly relied on in establishing the degree of

complexity of these derivatives. Elementary analysis is obviously of little assistance, and the presence of so many hydroxyl groups rendered accurate determinations of molecular weight impossible, especially as water was the only solvent that could be employed.

Experimental.

The same method of preparation was adopted in each case. Ten grams of finely powdered sugar were added gradually to 50 c.c. of methyl alcohol containing 0·25 per cent. of hydrogen chloride, and the mixture was gently warmed, if necessary, to hasten solution. The solution was then concentrated on a steam-bath to a viscid syrup, which was dissolved in a small quantity of methyl alcohol, and, after the solution had been filtered, absolute alcohol was added, which precipitated the complex as a white, amorphous product. This was collected with difficulty, owing to the deliquescent nature of these compounds, and finally dried to constant weight at 70—80°/12 mm.

Methyltetragalactoside.—Found: C=44·16; H=6·8; OMe=4·3, 4·0.

$C_{25}H_{44}O_{21}$ requires C=44·12; H=6·5; OMe=4·5 per cent.
$[\alpha]_D$ in water=94·0° (c=1·6590).

Hydrolysis of Methyltetragalactoside.—On heating at 100° with N/100-hydrochloric acid, the specific rotation increased to the constant value +108·5° at the end of five hours. Galactosephenylosazone alone was isolated at this stage, so that the increase in optical activity is probably due to the presence of α-methylgalactoside. Thereafter, the acid concentration was raised to N/10, and some of the polarimetric changes observed are shown below:

Initial specific rotation............	+108·5°
After 320 minutes at 100°	108·5
" 340 " "	106·0
" 360 " "	100·0
" 420 " "	94·0
" 540 " "	86·8 (constant)

As in the case of methyldigalactoside, the presence of β-methylgalactoside seems established by the fluctuations in activity recorded in the first sixty minutes. The final optical value when corrected for the calculated weight of sugar formed on the basis of the suggested formula for the compound becomes +82·0° (galactose= +81·0°).

Methyltetraglucoside.—Found: C=43·5; H=6·6; OMe=4·96.
$C_{25}H_{44}O_{21}$ requires C=44·12; H=6·5; OMe=4·5 per cent.
$[\alpha]_D$ in water=98·1° (c=0·9070).

Hydrolysis of Methyltetraglucoside.—The specific rotation increased on partial hydrolysis with $N/100$-acid at 100° to the value +104·5° at the end of sixty minutes, and then declined steadily, the final value, +87·5°, being reached at the end of four hours. The initial rise and subsequent fall probably indicate, as in the case of the galactose derivative, that both α-methylglucoside, $[\alpha]_D+157°$, and β-methylglucoside, $[\alpha]_D-33°$, are present. On completing the hydrolysis with $N/10$-acid, the optical activity continually declined, reaching the constant value +57·3° after heating for a further six hours. Calculating on the above formula, this gives +54·1° as the actual value for the specific rotation, which again is not far removed from the theoretical number +52·5°.

Methyltrimaltoside.—This compound, even after drying to constant weight at 70°/40 mm., retained a molecule of water, which was only removed on further heating at 100°/40 mm.

Found: C = 43·0, 43·0; H = 6·6, 6·7; OMe = 3·6, 3·5; H_2O = 1·5.

$C_{37}H_{64}O_{21},H_2O$ requires C = 43·4; H = 6·5; OMe = 3·0; H_2O = 1·7 per cent.

$[\alpha]_D$ in water +124·0° (c = 1·057).

Hydrolysis of Methyltrimaltoside.—After heating with $N/100$-hydrochloric acid at 100° for three hours, the specific rotation had declined to the constant value +113·6°, when maltosephenylosazone was isolated, but on further hydrolysis with $N/10$-acid the activity continued to decline, showing that both the maltoside and the maltose were undergoing hydrolysis. The final value, +56·8° (corrected, +53·7°), was obtained at the end of ten hours.

The author desires to express her thanks to Professor Irvine for the advice and assistance which she has received.

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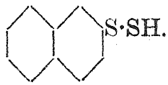
[*Received, March* 12*th*, 1918.]

L.—*The Preparation of a New Type of Organic Sulphur Compound.*

By Gerald Noel White.

The compound which forms the subject of this paper is a representative of a class of compounds which, so far as can be ascertained, has hitherto eluded isolation, being a derivative of hydrogen persulphide, H_2S_2, in the form of *β-naphthylthiosulphoxylic acid*:



It is highly probable that compounds of this type are produced as intermediate products in a number of chemical processes. In particular, the production of the sulphide dyes in all probability involves the formation of analogous derivatives of hydrogen disulphide.

The compound in question is produced by gently heating together molecular quantities of β-naphthyl disulphide, sodium sulphide crystals, and pure sulphur. After complete solution of the sulphur in the aqueous sodium sulphide, the naphthyl disulphide passes slowly into solution with continued heating to about 80°.

On cooling, glistening lamellæ of the *sodium* salt, which is very readily soluble in water, crystallise out. Purification is difficult, but after pressing on a porous plate, the most satisfactory method is to dissolve the sodium salt in alcohol and precipitate it with benzene.

For analysis, a portion of the sodium salt prepared in this way was treated with aqueous hydrochloric acid. The free acid was dissolved in alcohol and precipitated with water; this process was repeated three times and the product dried in a desiccator:

0·1757 gave 0·4044 CO_2 and 0·0569 H_2O. C=62·8; H=3·6.
0·1136 gave 0·2827 $BaSO_4$. S=34·1.
$C_{10}H_8S_2$ requires C=63·1; H=3·2; S=33·7 per cent.

With lead acetate, a deep orange precipitate is obtained, which darkens to scarlet on keeping, and ultimately changes to deep brown or black by decomposition to lead sulphide.

If this reaction is allowed to proceed in boiling alcohol, and the clear solution decanted quickly, crystals of β-naphthyl disulphide are formed on cooling which are remarkable for their purity. A study of this reaction failed to detect any deposition of sulphur as should result from the decomposition of a normal

lead salt, and it seems probable that the alcohol used in the reaction may act as a reducing agent, which would explain this observation.

At present, however, the evidence is insufficient to do more than indicate the possible course of the reaction.

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[*Received, June 11th*, 1918.]

LI.—*Double Carbonates of Sodium and Potassium with the Heavy Metals.*

By MALCOLM PERCIVAL APPLEBEY and KENNETH WESTMACOTT LANE.

THE combination of alkali carbonates with carbonates of the heavy metals to form crystalline double salts has been long known, many of these compounds having been prepared by Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 75) by digesting the precipitated metallic carbonate with excess of a concentrated solution of the alkali carbonate. Double carbonates of cobalt, nickel, zinc, and magnesium with potassium, and of copper, magnesium, cobalt, nickel, and zinc with sodium, were thus prepared, whilst several double bicarbonates were obtained in a similar manner. Owing to the method of preparation adopted, Deville's compounds must have been contaminated with normal and basic metallic carbonates, but his products were sufficiently pure to make possible a general characterisation of this group of substances. A somewhat more satisfactory method of preparation was adopted by Reynolds (T., 1898, **73**, 262), who ground the solid acetate of the metal with a concentrated solution of potassium carbonate. Under these conditions, complete solution takes place, and the crystalline double carbonate is subsequently deposited in a fairly pure state. In this way, Reynolds succeeded in obtaining the double carbonate of copper and potassium which Deville had failed to prepare owing to its great solubility. The analyses of Reynolds's copper compounds show rather high values for the copper content, and suggest the presence of basic carbonate. Gröger (*Ber.*, 1901, **34**, 429) afterwards demonstrated the advisability of adding bicarbonate to the alkaline carbonate solution, a modification which, as was pointed out by Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 71), represses the hydrolytic dissociation of the copper carbonate. The potassium and sodium copper carbonates prepared by Gröger never-

theless contained considerable amounts of basic carbonate, the potassium salt being particularly impure. This was, however, probably due to the subsequent treatment of the salts.

The nature of the deep blue solutions from which the copper salts are deposited has been examined by Luther and Kršnjavi (*Zeitsch. anorg. Chem.*, 1905, **46**, 170), who proved by transport experiments the presence of a deep blue complex negative ion containing copper. The conditions under which crystallisation of double salts from such solutions takes place have also been discussed by Deville and by Gröger. No quantitative study of these conditions has yet, however, been attempted, although the case is one of particular interest, since it relates to a double salt of which one constituent is practically insoluble in water. The authors therefore undertook a study of the solubility equilibria in the case Na_2CO_3–$Na_2Cu(CO_3)_2$–$CuCO_3$, which is typical of double salt equilibria of this kind. It was hoped that a parallel investigation of the equilibria in the formation of the potassium cobalt compound would be of interest. Unfortunately, owing to the difficulties of analysis in the latter case and to the enforced suspension of the work under present conditions, it has not been found possible to bring this part of the investigation to a satisfactory conclusion. The present communication therefore deals almost entirely with the sodium copper carbonate equilibrium.

Preparation and Properties of the Double Salts.

The salts prepared for the purpose of this investigation were all obtained by a method which, whilst not giving so good a yield as could be obtained by Reynolds's method, was preferable for the purpose in view, since it gave products of greater purity, analysis showing that the amount of basic carbonate present was small.

Sodium Copper Carbonate.—A solution was prepared containing about 100 grams of sodium carbonate (anhydrous) and 40 grams of sodium bicarbonate in a litre. To this solution, at a temperature of about 50°, a concentrated solution of cupric acetate was added from a burette with a fine point, the liquid being stirred continually during the addition. A clear, deep blue solution quite free from suspended basic carbonate is obtained in this way. The amount of cupric acetate solution to be added is found by trial; if too much is added, precipitation of basic carbonate occurs; if too little, there is no crystallisation. The solution is filtered and left to remain overnight, when a deposition of well-formed crystals of the double salt takes place. These are collected, rapidly washed with

pure alcohol, and dried in a desiccator. The mother liquor can be used for a further preparation, and gives a rather better yield.

The salt, which crystallises in needles or rosette-like agglomerations, dries to a constant weight in a desiccator. It is, in fact, a more stable substance than might be expected, since microscopic examination fails to show any alteration in the transparency of the crystals after they have been kept at the temperature of boiling water for a considerable time. At higher temperatures, the substance loses water and carbon dioxide, passing through a stage when it has a purple colour, and giving finally a mixture of cupric oxide and sodium carbonate. It is decomposed by water, but dissolves in and can be recrystallised from a concentrated solution of sodium carbonate containing bicarbonate. This observation, which is in direct contradiction to the experience of Gröger (*loc. cit.*), has been fully established by repeated tests.

The copper in the compound was determined by the sulphide method and also electrolytically, the sodium as sulphate after precipitation of the copper. Carbon dioxide and water were estimated directly in the usual manner.

Found: $Cu = 22{\cdot}05$; $Na = 16{\cdot}05$; $CO_3 = 42{\cdot}52$; $H_2O = 19{\cdot}62$.
$Na_2Cu(CO_3)_2,3H_2O$ requires $Cu = 22{\cdot}40$; $Na = 16{\cdot}21$; $CO_3 = 42{\cdot}37$; $H_2O = 19{\cdot}02$ per cent.

It will be seen that the substance has the formula

$$Na_2Cu(CO_3)_2,3H_2O,$$

as was found by Deville, Gröger, and Wood and Jones (*loc. cit.*). The amount of water of crystallisation in this salt is somewhat anomalous, as the large number of double carbonates of potassium investigated by Reynolds, and the sodium cobalt compound to be described later, all crystallise with four molecules of water.*

Sodium Cobalt Carbonate.—This substance was prepared in exactly the same manner as the copper compound, except that the cobalt was added in the form of nitrate solution. The double salt crystallises in crusts of fine crystals of a very bright reddish-purple colour. It can be recrystallised from a solution of sodium carbonate and bicarbonate, but it is difficult to obtain well-formed crystals.

The salt was analysed by dissolving a weighed quantity in excess of standard acid and titrating with standard alkali, using methyl-orange as indicator. The colour of the solution is not sufficiently intense to affect the accuracy of this determination, which gives the total basic equivalent of the sodium and cobalt in the compound. Another weighed sample is then ignited until it is completely con-

* The potassium copper salt can also be obtained anhydrous and with one molecule of water, but not with three.

verted into a mixture of cobalt oxide and sodium carbonate, of which the latter can be extracted with hot water and estimated by titration. This gives the percentage of sodium in the compound and the percentage of cobalt by comparison with the determination of total basic value. The sodium was also determined as sulphate (*a*). The water was determined in the usual way and the carbon dioxide by difference.

Found: Co = 20·42; Na = 15·03, 15·26(*a*); CO_3 = 40·79; H_2O = 23·64.

$Na_2Co(CO_3)_2,4H_2O$ requires Co = 19·85; Na = 15·52; CO_3 = 40·38; H_2O = 24·25 per cent.

The substance evidently has a formula corresponding with the double potassium salts described by Reynolds, and is therefore unlike the sodium copper carbonate, which has only three molecules of water of crystallisation. Deville also obtained a double sodium cobalt carbonate with ten molecules of water, but this substance was not formed under the conditions described in this paper.

Potassium Cobalt Carbonate.—This salt is obtained in an analogous manner to those previously described, the solution used for the preparation containing about 400 grams of potassium carbonate and 100 grams of potassium bicarbonate per litre. On addition of cobalt nitrate solution, a dark, reddish-purple solution is obtained very similar in appearance to that from which the sodium salt is deposited. The crystalline double salt is, however, different in habit and in appearance from the corresponding sodium compound. The crystals are well formed and do not mass together in compact crusts. They present the appearance of six-sided tables which have not the bright purple tint of the sodium salt. Large crystals formed by evaporation of solutions saturated with the double salt have a red colour resembling ordinary cobalt compounds, whilst the smaller crystals deposited from the purple solutions are a lighter red, or in some cases a pale pink. The differences in colour between different specimens at first led to the belief that the cobalt potassium compound occurred in several forms differing either in composition or in crystalline form. Repeated analyses and measurements of solubility failed, however, to show any difference between the differently coloured specimens, nor did either the red form or the pink form grow at the expense of the other when both were kept in contact with a saturated solution for several months. The authors are therefore bound to conclude that the differences of colour referred to are not due to differences of composition, structure, or crystalline arrangement. They are probably to be explained by occlusion of different amounts of some colloidal substance, such as cobalt

carbonate. This conclusion is supported by the observation that increase in the concentration of bicarbonate in solution tended to favour the production of the lighter coloured variety. The effect is probably quite parallel with the well-known changes in the colour of many metallic salts when crystallised from solutions of varying acidity; these changes have been shown to be due to the occlusion of varying quantities of metallic hydroxides under different conditions.

Analysis by the method used for the sodium cobalt compound gave:

Found: $Co = 17 \cdot 85$; $K = 24 \cdot 05$; $CO_3 = 21 \cdot 60$; $H_2O = 36 \cdot 50$.

$K_2Co(CO_3)_2,4H_2O$ requires $Co = 17 \cdot 91$; $K = 23 \cdot 72$; $CO_3 = 21 \cdot 89$; $H_2O = 36 \cdot 45$ per cent.

This substance also clearly belongs to the normal type with four molecules of water of crystallisation, as was previously found by Reynolds.

Both the sodium and potassium cobalt salts have properties very similar to those of the sodium copper carbonate. They are quite stable in the cold, but lose water and carbon dioxide on heating. They are decomposed by water, but, like the copper compound, can be recrystallised from concentrated solutions of alkali carbonate and bicarbonate.

Formation of the Double Salts.

The formation of the double salts from the intensely coloured solutions has already excited some interest. Deville remarked upon the deep colour of the solutions, and doubted whether this colour could possibly be due to the small quantity of double carbonate which in the solid state is not more highly coloured than ordinary copper salts. A very striking experiment illustrating Deville's argument consists in acidifying a solution of the double carbonate containing 0·1 to 0·2 gram of copper per litre. This solution, which is bright blue, becomes almost colourless when the complex ion is destroyed by acidification, and even the addition of ammonia only produces a colour very much fainter than that of the original solution. Deville was so much impressed with the intense colour of the solutions that he regarded it as possible, if not probable, that the solutions contained some substance much more intensely coloured than the double carbonate into which it was slowly transformed during the crystallisation of the latter.

Other phenomena now to be discussed give considerable support to Deville's hypothesis. The crystals of the double salt are formed slowly from the solution when the latter has been kept for several hours, but the solution is not supersaturated in the ordinary sense.

This is shown by the fact that addition of crystalline nuclei does not appreciably hasten the separation. Gröger, who noted this phenomenon, also describes a remarkable experiment, which the authors have been unable to confirm. According to him, if a solution supersaturated with sodium bicarbonate is used in the preparation of the copper solution, addition of the crystalline double salt brings about no crystallisation, but sowing with a fragment of sodium bicarbonate not only induces crystallisation of the bicarbonate itself, but also brings about the rapid separation of the double salt along with it. This would constitute a remarkable type of supersaturation; attempts to repeat the experiment, however, never led to the result described, only bicarbonate being obtained as solid phase, whilst no appreciable fall in copper concentration took place.

It was thought that evaporation or absorption or loss of carbon dioxide might be a determining factor. Experiments were therefore entered on to test these points, but the results were entirely negative. Whether the solutions were left to crystallise in the open, in sealed flasks, or in a desiccator connected to a Kipp's apparatus for carbon dioxide, no appreciable difference in the rate of crystallisation was observed. It is therefore tentatively suggested that the behaviour of the solutions is due to one of the following causes:

(1) The rate of crystallisation is very small, and there are no stable supersaturated solutions.

(2) An intermediate compound is formed in the solutions which changes only slowly into the practically insoluble double salt.

In the latter case, the change from intermediate compound to double salt is reversible, since the double salt can be recrystallised from a solution of carbonate and bicarbonate.

The Solubility Equilibria.

In undertaking this investigation, the authors were faced at the outset with the difficulty that solutions of the double salts are unstable in absence of bicarbonate. Repeated attempts to obtain a solution saturated with sodium carbonate decahydrate and with the sodium copper carbonate in absence of bicarbonate all led to failure. When the solids were stirred in a constant-temperature bath at 18°, a blue solution was obtained, but decomposition with precipitation of basic compounds always occurred before the experiment had proceeded a sufficiently long time to ensure the attainment of equilibrium. It was therefore decided that the work must be carried out exclusively with solutions containing bicarbonate.

In many respects, the simplest plan and that promising results of most interest was to work with solutions saturated with sodium carbonate or with sodium bicarbonate, and the determinations made by the authors relate only to such solutions. The equilibria investigated are therefore those of (1) sodium copper carbonate and sodium bicarbonate with solutions containing increasing quantities of sodium carbonate; (2) sodium copper carbonate and sodium carbonate decahydrate with solutions containing decreasing quantities of bicarbonate. In each of these regions we are dealing with a system univariant at constant temperature with two solid phases. At the point of intersection we have at constant temperature a non-variant system with three solid phases.

The concentration of copper in the equilibrium solutions is in all cases very small in comparison with the concentrations of the sodium salts. The latter may consequently be considered as influenced only to an inappreciable extent by the presence of copper. The determinations therefore serve also to characterise the equilibrium of sodium carbonate and sodium bicarbonate at the temperature of experiment. They may be compared with the results of McCoy and Test (*J. Amer. Chem. Soc.*, 1911, **33**, 473) at 25°.

The solutions were prepared in a stirring-bottle closed with a mercury seal and maintained at 18° by means of a constant-temperature bath regulating to 0·02°. The time allowed for equilibrium to be established was never less than forty hours, preliminary experiments having shown that this was a satisfactory minimum period. When saturation was complete, the stirrer was stopped and the solution was allowed to settle. The stirrer was then removed and replaced by an inverted filter, through which the saturated solution was blown into a clean flask, from which samples were taken for analysis. Filtration of the solutions was necessary, as in some cases a solid substance, probably a basic carbonate, was present in a state of very fine suspension.

The concentration of copper in the solutions was found by direct titration of the solutions with a potassium cyanide solution, standardised against alkaline copper solutions of known strength, due allowance being made for the variation in the titre of the solutions ocasioned by variation in bicarbonate concentration. The cyanide titration of these solutions is much sharper than in the case of ammoniacal copper solutions of equal copper content (*Analyst*, 1918, **43**, 268).

The carbonate and bicarbonate were determined by dilution of the solutions by means of carefully standardised pipette and flask, and titration by Winkler's method. A modification of this method

which proved serviceable consisted in running in $N/10$-sodium hydroxide solution until the bicarbonate was almost completely changed into carbonate, the amount necessary being found by a preliminary trial. Excess of neutral barium chloride solution and a drop of phenolphthalein were then added, and the titration with sodium hydroxide was completed. This modification is preferable in point of convenience to Winkler's method of adding excess of sodium hydroxide, then adding barium chloride and phenolphthalein, and titrating back, and appears to be quite as accurate, although, of course, several titrations of each solution must be carried out. If the quantity of sodium hydroxide solution first added is sufficiently near the quantity required for complete conversion (within 0·2 or 0·3 c.c.), there appears to be no difficulty occasioned by the decomposition of the barium bicarbonate which must be formed on adding barium chloride.

The following tables give the results of the several experiments made with the sodium copper solutions (table I) and with the potassium cobalt solutions (table II). No determinations of the cobalt content of the latter solutions are given, as sufficiently trustworthy values were not obtained at the time when the experiments were interrupted. The concentration of cobalt in the equilibrium solutions was in the neighbourhood of 0·1 to 0·2 gram per litre, and appeared to pass through a minimum value at a concentration of potassium carbonate equal to about 200 grams per litre. A similar variation is not found in the case of the sodium copper compound, with which the copper content of the equilibrium solutions increases continually with increase of the carbonate concentration.

TABLE I.

No. of experiment.	Hours stirring.	Solid phases.	Na_2CO_3 grams/litre.	$NaHCO_3$ grams/litre.	Cu grams/litre.
1	48	$Na_2Cu(CO_3)_2,3H_2O$ and $NaHCO_3$	9·27	87·79	—
2	140		11·08	86·45	0·0509
3	50		11·29	86·75	—
4	50		13·44	85·27	0·0542
5	50		37·36	78·63	—
6	100		61·32	74·18	—
7	100		62·36	72·65	0·0870
8	100		96·68	65·31	0·1061
9	50		99·30	64·10	0·1061
10	70		152·63	56·24	0·1411
11	50		168·75	53·60	0·1553
12	50	$Na_2Cu(CO_3)_2,3H_2O$ $NaHCO_3$ and $Na_2CO_3,10H_2O$	185·02	53·77	—
13	50	$Na_2Cu(CO_3)_2,3H_2O$ and $Na_2CO_3,10H_2O$	193·13	17·64	—
14	50		195·57	7·48	—
15	50		197·08	18·94	0·257

TABLE II.

No. of experiment.	Hours stirring.	Solid phases.	K_2CO_3 grams/litre.	$KHCO_3$ grams/litre.
1	120		13·3	280·6
2	70		14·85	282·5
3	50		25·5	272·4
4	240		47·5	262·3
5	100		103·2	237·0
6	70		114·1	230·7
7	40		125·1	227·6
8	50	$K_2Co(CO_3)_2,4H_2O$ and $KHCO_3$	145·7	219·0
9	120		166·8	203·2
10	120		220·0	181·0
11	120		289·4	158·9
12	70		309·2	151·3
13	40		453·5	108·4
14	70		607·7	68·9
15	120		643·0	64·1
16	120		704·3	54·6
17	120	$K_2Co(CO_3)_2,4H_2O$, $KHCO_3$ and $K_2CO_3,2KHCO_3,3H_2O$	800·2	43·1
18	120	$K_2Co(CO_3)_2,4H_2O$ and	805·1	40·9
19	170	$K_2CO_3,2KHCO_3,3H_2O$	822·8	35·0
20	170	$K_2Co(CO_3)_2,4H_2O$, $K_2CO_3,2H_2O$ and $K_2CO_3,2KHCO_3,3H_2O$	825·8	33·1
21	100	$K_2Co(CO_3)_2,4H_2O$ and $K_2CO_3,2H_2O$	836·2	12·2
22	170		840·8	5·9

These results are represented graphically in Figs. 1 and 2. Fig. 1, which also contains McCoy and Test's results for the sodium carbonate–bicarbonate equilibrium at 25°, shows no sign of a break corresponding with the double compound $Na_2CO_3,NaHCO_3,2H_2O$ (trona) at 18°. It is therefore probable that this compound ceases to be stable in contact with solutions at some temperature between 18° and 25°.

In the course of the solubility experiments, it was noted that a distinct change in the appearance of the solid phase occurred in passing along the bicarbonate curve. The bicarbonate used in these experiments was the usual micro-crystalline variety, and this form appeared to suffer no change when left in the stirring bottle in contact with solutions ranging from pure bicarbonate to a point on the curve corresponding with about 70 grams of carbonate per litre. Beyond this point, the solid phase becomes transformed into well-formed, transparent crystals. These crystals are nevertheless pure anhydrous bicarbonate, as was established by repeated analyses. It is possible that a polymorphic change takes place, but in view of the fact that the solubility curve shows no break, and seeing that all attempts to obtain evidence of a definite transition point failed completely, the authors are inclined to think that the pheno-

menon is not to be explained by polymorphism. This opinion is supported by the absence of any clear distinction between the two

FIG. 1.

Upper curve, McCoy and Test, 25°
Lower „ Applebey and Lane, 18°.

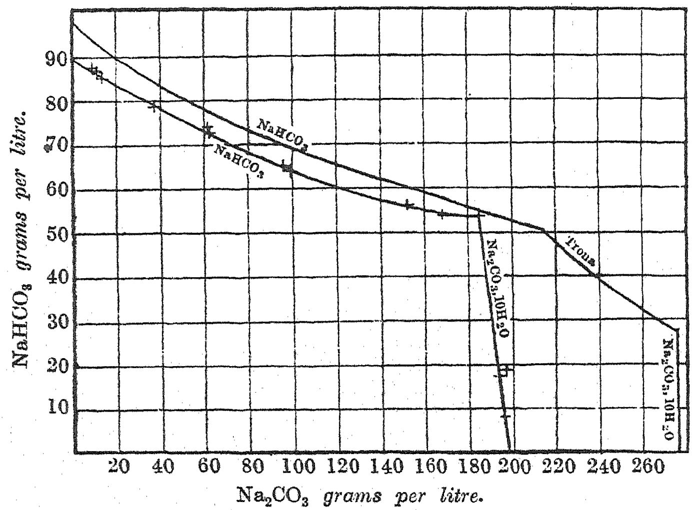
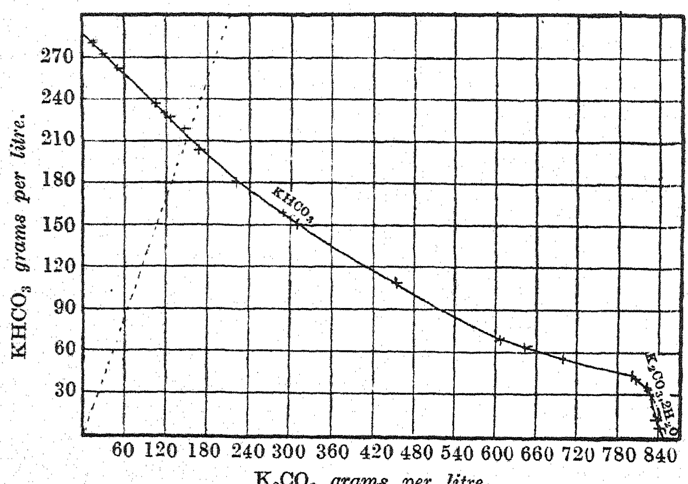


FIG. 2.



kinds of crystals when examined under the polarising microscope. Probably the conditions of the solubility equilibrium in presence

of considerable quantities of sodium carbonate are such as to facilitate the growth of the crystals.

Fig. 2, which is the corresponding diagram for potassium carbonate and bicarbonate, shows clear evidence of a double compound. This substance, the region of stability of which is very limited at 18°, is doubtless identical with the compound obtained by Bauer (*Ber.*, 1883, **16**, 1143) during the evaporation of bicarbonate solutions on a large scale in a mineral water factory. This salt was carefully analysed, and was examined crystallographically by Rammelsberg, but all attempts to obtain it synthetically have up to the present failed. Its formula is

$$K_2CO_3,2KHCO_3,3H_2O,$$

and, as the figure shows, it is only obtainable in equilibrium with a very limited range of solutions, which are very different in composition from the double salt itself.

The determinations of copper concentration in the equilibrium solutions lie on a smooth curve showing a steady increase with increase in the concentration of sodium carbonate. The copper determination of experiment 15 alone lies considerably above the curve. This point is the only determination of copper concentration in a solution in equilibrium with sodium carbonate decahydrate as solid phase, and seems to show that the rapid decrease in the bicarbonate concentration along the decahydrate curve brings about an increase in the copper content. Experiment 15 is, however, not very satisfactory, as the solution appears to have been somewhat supersaturated with carbonate owing to failure of the regulation of temperature, and the corresponding point lies at a considerable distance from the curve in Fig. 1 which connects the other points. The authors therefore content themselves with noting the observation, but lay no stress on its interpretation.

Discussion of Results.

The experimental results set forth above have several features of interest which throw some light on the nature of the equilibria involved. In the first place, it is noteworthy that the curve of copper concentrations does not approach the solubility of copper carbonate in water, which is negligibly small, as the concentration of sodium carbonate decreases, but the curves of solubility of copper carbonate and double salt appear to intersect at a copper concentration of about 0·045 gram per litre. This is unlike the normal case of double salt equilibrium in which the solubility of each component is lowered by the addition of the other. Assuming that this abnormal rise of solubility of copper carbonate in the presence

of sodium carbonate is due to the formation of the complex ion $Cu(CO_3)_2$, it is easily shown that the first effect of sodium carbonate must be to depress the solubility of the other component, the solubility passing through a minimum, and subsequently rising on addition of further quantities of the sodium salt. The investigation of this curve forms no part of the present investigations. It may be noted, however, as a point of interest, that by the application of the mass-action law, which is possibly justifiable in that only very dilute solutions are under consideration, it can be readily established that the position of the minimum solubility is given by the condition.

$$[Cu^{\cdot\cdot}]=[Cu(CO_3)_2'']$$.

Passing now to the consideration of solutions saturated with the double salt, $Na_2Cu(CO_3)_2,4H_2O$, the results obtained in the present work are again at variance with the normal behaviour of double salts in that the increase of concentration of one component brings about an increase in the concentration of the other, the curve apparently rising throughout its whole course. This abnormal behaviour must, as in the case of the solubility of copper carbonate itself, be occasioned by the formation of a new constituent in the solution which removes copper from the solution equilibrium of the double salt, and so leads to an increase in its apparent solubility. The increasing solubility of the double salt with rising concentration of sodium carbonate thus constitutes a direct experimental proof of the view held by Deville that the copper in these solutions was largely present in some form chemically different from the salt which crystallises out.

Turning now to the identification of the dissolved substance, which is thus the parent of the crystalline double carbonate, a little consideration will show that if the substance is an ionisable one, the complex copper ion which forms the negative part must consist of a more heavily carbonated species, such as $Cu(CO_3)_4''''''$; the concentration of such an ion would increase with increasing concentration of carbonate. On the other hand, if such ions are present, it is very remarkable that double salts containing more than one equivalent of alkali carbonate to one of metallic carbonate never crystallise out of any of these alkali metallic carbonate solutions.

The authors are, however, of opinion that the true explanation of the solubility phenomena is to be found in the presence of a large proportion of the copper in the form of a colloidal substance, probably a normal or basic copper carbonate. This view accounts for the contrast between the colour of the solutions and that of the crystalline double salts, and is supported by the fact that

coagulation can certainly be brought about, although with difficulty, by the addition of much sodium phosphate to the solutions. The possibility that the solutions are of a colloidal nature has already been considered and rejected by Luther and Kršnjavi (*loc. cit.*) on the evidence of their transport experiments, and also because the solutions can diffuse through a parchment membrane. It appears, however, that such arguments, whilst they prove the presence of complex negative ions containing copper, do not at all exclude the simultaneous presence of a positive colloid, which may, in fact, be much greater in amount than the complex ions. In fact, it is obvious that when a solution contains a colloidal substance in kinetic equilibrium with crystalloids, the colloid will diffuse through an animal membrane by first changing into the dialysable form, the colloidal form being again obtained on the other side of the membrane by the reverse change. The passage of such a solute through a membrane will doubtless be slow in comparison with the rate of dialysis of crystalloids, but when the above conditions are fulfilled, such passage must take place. The escape of colloid normally comes to an end after a small quantity has passed, owing to the disappearance of some crystalloid factor on which the change to crystalloid form depends. An example which will make the argument clear may be found in ferric chloride. A solution of this substance may be regarded as made up of colloidal ferric hydroxide, ferric ions, and hydrogen and chlorine ions. In the dialyser, the ions, including the ferric ions, immediately begin to diffuse out, and diffusion of ferric ions will, in fact, continue as long as chlorine ions remain in the solution. The concentration of chlorine ions in such a solution is, however, not very great, and their escape is fairly rapid. The result is that escape of ferric ions soon comes to an end. In the case of the alkaline copper solutions, however, the crystalloid and diffusible substance, $Na_2Cu(CO_3)_2$, is constantly regenerated, since the solutions contain much sodium carbonate, which takes a considerable time to escape from the dialyser. The escape of copper is therefore more pronounced than that of iron from a ferric chloride solution, and, in fact, is so favoured by the presence of excess of sodium carbonate that the solution simulates the behaviour of a simple crystalloid.

It is perhaps worth noting that Luther and Kršnjavi remark that the movement of the coloured boundary in their transport experiments was very slow. This may to some extent be due to the conversion of the complex ions which have crossed the boundary into the positive colloid, which travels in the opposite direction by cataphoresis.

In conclusion, the authors wish to express their indebtedness to Mr. D. H. Nagel and to Mr. D. L. Chapman for much valuable assistance and advice during the progress of this work. They have also to thank Mr. S. G. Plant for assistance in carrying out some of the analytical work.

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LII.—*The Constitution of Carbamides. Part VI. The Mechanism of the Synthesis of Urea from Urethane.*

By Emil Alphonse Werner.

The formation of urea from the interaction of ammonia and urethane (ethyl carbamate) has always been considered to afford conclusive evidence in support of the 'carbamide' structure, and is commonly represented by the equation:

$$CO(OEt)_2 + 2NH_3 = CON_2H_4 + 2EtOH.$$

This synthesis of urea is invariably assumed to be analogous to the formation of acetamide from ethyl acetate, urethane being merely recognised as the normal intermediate product.

As a matter of fact, it is nothing of the kind.

When the true mechanism of the change is brought to light, it is seen to be nothing more than a modification of Wöhler's synthesis, namely, the formation of urea from the union of ammonia and cyanic acid in the keto-form.

Properties of Urethane, and the Conditions under which Urea is formed from the Ester.

The vapour density of urethane (b. p. 182°) at 202·8° (b. p. of *m*-cresol) was found to be 43·22, whilst theory requires 44·5; on the other hand, when the ester was boiled under reflux, it was gradually dissociated in accordance with the equation

$$EtO\cdot CO\cdot NH_2 \longrightarrow \underset{\text{(polymerised)}}{HCNO} + EtOH;$$

thus, after two hours, 16 per cent. of the theoretical yield of cyanuric acid was obtained.

The decomposition of the ester by alkali in aqueous solution was found to proceed on the same lines: the change is not a direct hydrolysis, as commonly stated in the literature, and may be represented thus:

$$(1)\ EtO{\cdot}CO{\cdot}NH_2 + NaOH \longrightarrow H_2O + EtO{\cdot}C(ONa){:}NH \longrightarrow NaOCN + EtOH.$$

$$(2)\ NaOCN + 2H_2O = NaHCO_3 + NH_3.$$

The following results were obtained when urethane and sodium hydroxide (both in $N/5$-solution) were heated at 100°:

Time in minutes.	Urethane decomposed, per cent.	Sodium cyanate formed, per cent.	Sodium carbonate formed, per cent.
5	50·9	32·9	18·0
15	62·5	37·25	25·25
30	63·95	29·70	34·25
60	66·80	28·80	38·0
90	71·0	17·0	54·0

At 15°, after three days, 18 per cent. of urethane was decomposed, with the formation of 5·5 per cent. of sodium cyanate and 12·5 per cent. of sodium carbonate. The change was therefore independent of dissociation of the ester (compare decomposition of urea, this vol., p. 88).

When urethane was heated in a current of hydrogen chloride, it was decomposed, thus:

$$EtO{\cdot}CO{\cdot}NH_2 + 2HCl = CO_2 + EtCl + NH_4Cl.$$

This decomposition of urethane in two different directions may be represented thus:

$$\underset{\text{(basic form)}}{EtO{\cdot}CO{\cdot}NH_2} \underset{\text{in presence of acid}}{\overset{\text{in presence of alkali}}{\rightleftarrows}} \underset{\text{(acidic form)}}{EtO{\cdot}C(OH){:}NH.}$$

Since urea is formed from the hydrolysis of cyanic acid, thus,

$$2HCNO + H_2O = CON_2H_4 + CO_2$$

(this vol., p. 95), it is necessary to reach the temperature of the dissociation of urethane in solution in order to obtain urea from it; thus, when the ester was heated in aqueous solution in a sealed tube for two hours at 130°, 5·94 per cent. of the theoretical yield of urea was obtained; after six hours, the yield was 16·62 per cent. (Expts. II and III). Whilst the presence of ammonia would obviously promote the change, the origin of urea in this synthesis is clearly revealed by these results, and is properly represented thus:

$$CO{<}^{NH_2}_{OEt} \longrightarrow \begin{matrix} EtOH \\ + \\ HNCO \end{matrix} + NH_3 \longrightarrow HN{:}C{<}^{NH_3}_{\underset{|}{}O}.$$

A comparative study of the formation of urethane and ammonia from the interaction of urea and ethyl alcohol (a change which is also regarded from a false point of view) has brought to light evidence in support of the above explanations; thus, when a 5*N*-alcoholic solution of urea was heated for two hours at 150°, 41·66 per cent. of the theoretical yield of urethane was formed, as against 33·3 per cent. yield of urea from the interaction of urethane and ammonia under similar conditions (Expts. V and VI).

The greater facility with which urea dissociates explains the higher result in the former case, which otherwise appears abnormal, since the formation of an amide from an ester and ammonia takes place with ease, as compared with the reverse reaction.

Urea is a relatively stable substance, and if it has the 'carbamide' constitution, the question may be asked why it is not formed from ethyl carbonate (or carbamate) with the same ease as undoubted diamides are formed from esters and ammonia; for example, no urea was produced after urethane had remained in contact with a considerable excess of ammonia solution for ten months at the ordinary temperature.

It has been generally accepted as an axiom that the system $:C(OH)_2$ cannot form part of a stable molecule; the author now ventures to maintain that the evidence all round is no less convincing as regards the system $:C(NH_2)_2$, and herein lies the true answer to the question just stated. Urea, thiourea, and guanidine are the only known stable substances that have been assumed to contain this system, and in the case of thiourea it is well known that when the thiocarbamic esters $H_2N\cdot CS\cdot OEt$ and $H_2N\cdot CS\cdot SEt$ respectively are heated with ammonia in alcoholic solution, ammonium thiocyanate is formed. Since the reaction is effected below the temperature at which this salt dissociates (a necessary preliminary for the formation of the isomeride), no thiourea is produced, a fact for which no explanation can be offered when the erroneous 'thiocarbamide' structure is assumed.

As regards guanidine (free base), its constitution has yet to be proved (compare Krall, T., 1915, **107**, 1398).

Experimental.

The results of the decomposition of urethane by sodium hydroxide in aqueous solution were obtained as follows. A mixture of 0·89 gram of urethane, 10 c.c. of *N*-sodium hydroxide, and 40 c.c. of distilled water was heated to the boiling point under reflux for the stated periods. After the solution had been rapidly cooled,

the 'carbonate' was precipitated by barium nitrate and barium hydroxide; the filtrate, after careful neutralisation with dilute nitric acid, was precipitated with $N/10$-silver nitrate, the excess of which was titrated by Volhard's method. Each experiment was made in duplicate.

The results were calculated on the basis:

0·89 Gram of urethane $\longrightarrow$ $BaCO_3 = 20$ c.c. N-HCl.
$NaOCN = 100$ c.c. $N/10$-$AgNO_3$.

Example.—After one hour, $BaCO_3$ precipitated required for neutralisation 7·6 c.c. N-HCl, $=38·0$ per cent. of the theoretical; NaOCN formed required for precipitation 28·8 c.c. $N/10$-$AgNO_3$, $=28·8$ per cent. of the theoretical.

Decomposition of Urethane by Hydrochloric Acid.

Expt. I.—Twenty grams of urethane were heated to 150—160° in a distillation flask, while hydrogen chloride was passed through the liquid; after a short time crystals began to separate, and the heating was maintained for half an hour. The gas which was evolved (1) burned with a green flame (ethyl chloride), and (2) gave a copious precipitate with excess of barium hydroxide solution (carbon dioxide). The product was treated with ether to remove all unchanged urethane, and the residue, which was readily and completely soluble in cold water, contained $Cl = 66·24$ (NH_4Cl requires $Cl = 66·35$ per cent.), and gave no reaction for cyanuric acid.

The evolved gas, when collected over warm water, was reduced to almost half its volume after treatment with sodium hydroxide, and the residual gas burnt more freely than before with a green flame. The decomposition was therefore in accordance with the equation given.

Formation of Urea when Urethane was Heated with Water.

Expt. II.—2·5 Grams of urethane and 7·5 c.c. of water were heated in a sealed tube for two hours at 130°. After evaporation of the solution to dryness at 100°, the residue was extracted with ether, when there remained 0·05 gram, which was proved to be urea by the urease test and other reactions.

Expt. III.—As before, but the heating was maintained for six hours. Half of the final residue gave, when decomposed by

alkaline sodium hypobromite, 24·28 c.c. N_2 at *N.T.P.*, equal to 0·14 gram of urea, or 16·62 per cent. of the theoretical. Urea nitrate was readily prepared for identification from the remainder.

Formation of Ethyl Allophanate from Urethane.

Expt. IV.—A solution of 5 grams of urethane in 20 c.c. of alcohol was heated in a sealed tube for three hours at 150°. After evaporation of the alcohol, the residue was extracted with ether, and the insoluble product (0·065 gram) crystallised from hot water in colourless needles melting at 191°, which was the melting point of a specimen of ethyl allophanate used for comparison. When heated with barium hydroxide solution, a copious precipitate of barium carbonate was formed after a few moments, a reaction characteristic of the ester. Whilst the yield was small, the result proves that dissociation of urethane must have taken place.

Quantitative Comparison of (a) *Interaction of Urea and Alcohol,* (b) *Interaction of Urethane and Ammonia.*

Expt. V.—A solution of 3 grams of urea in 10 c.c. of alcohol (urea = 5*N*) was heated in a sealed tube for two hours at 150°; from the product, after evaporation of the alcohol and extraction with ether, 1·75 grams of urea were recovered, whilst 1·85 grams of urethane were obtained from the ethereal extract. As 3 grams of urea are equivalent to 4·45 grams of urethane, the yield of the latter was 41·6 per cent. of the theoretical.

Expt. VI.—A solution of 4·45 grams of urethane in 10 c.c. of alcohol (urethane = 5*N*) which contained 0·85 gram of ammonia was heated as in the last experiment. One gram of urea was obtained after extraction of the residue with ether. Hence the yield was equal to 33·3 per cent. of the theoretical.

A determination of the vapour density of urethane by V. Meyer's method at 202·8° gave the following result: 0·0763 gram gave 21·2 c.c. at 14·5° and 741·45 mm. (corrected), whence V.D. = 43·22. Hence there was no dissociation under this condition.

Summary.

(1) Urethane is not directly hydrolysed when heated with sodium hydroxide in aqueous solution, as commonly stated; alkali cyanate is first formed, and then hydrolysed.

(2) The formation of urea when urethane (or ethyl carbonate) is heated in solution with ammonia is solely dependent on the dissociation of urethane, and is no more than a repetition of Wöhler's synthesis in a modified form.

(3) A comparison of the reaction with the formation of urethane from urea and alcohol supplies evidence which is opposed to the 'carbamide' formula.

(4) Attention is directed to a rational inference from the facts, namely, that the system $:C(NH_2)_2$ cannot form part of a stable molecule.

The author desires to express his thanks to Miss M. Coade, B.Sc., for her assistance in conducting part of the experimental work.

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LIII.—*The Abnormality of Strong Electrolytes. Part II. The Electrical Conductivity of Non-aqueous Solutions.*

By JNANENDRA CHANDRA GHOSH.

IN a previous paper it has been shown that in aqueous solutions of strong electrolytes, the increase in molecular conductivity with dilution can be accounted for quantitatively on the basis of the following simple assumptions:

(*a*) Only ions exist in solution, the force of attraction between oppositely charged ions being governed by the law of inverse squares.

(*b*) In solutions of binary electrolytes, the arrangement of ions is analogous to the marshalling of atoms in a simple cubic crystal, whilst that of the ions in solutions of ternary electrolytes corresponds with the fluorspar lattice.

(*c*) The oppositely charged ions of a molecule form electrically saturated neutral doublets.

(*d*) It has been shown that, on the above hypothesis, the work necessary to separate the constituent ions of a gram-molecule of univalent binary electrolytes to an infinite distance,

$$A = \frac{NE^2\sqrt[3]{2N}}{D\sqrt[3]{V}},$$

where N is Avogadro's number, E the charge on an ion, D the dielectric constant of the solvent, and V the molecular dilution. For a ternary electrolyte like barium chloride,

$$A = \frac{3NE^2 . 2 . \sqrt[3]{2N}}{D . \sqrt{3} . \sqrt[3]{V}}$$

(*e*) From Maxwell's equation of the distribution of velocities, it can be easily proved that the number of free ions in a solution containing a gram-molecule

$$= nN . e^{-\frac{A}{n.RT}},$$

where n is the number of ions into which a molecule dissociates.

(*f*) Since molecular conductivity is proportional to the number of free ions, and since $A = 0$ at infinite dilution,

$$\frac{\mu_v}{\mu_\infty} = \frac{n . N . e^{-\frac{A}{nRT}}}{nN} = e^{-\frac{A}{nRT}}.$$

In this paper it will be shown that the above equation, which gives very good results in the case of aqueous solutions, can be applied with equal success to non-aqueous solutions of strong electrolytes.

The organic ionising solvents have been arranged by Walden in the following order: (1) alcohols, (2) aldehydes, (3) acids, (4) acid anhydrides, (5) acid chlorides, (6) esters, (7) acid amides and amines, (8) nitriles, (9) thiocyanates, (10) thiocarbimides, (11) nitro-compounds, (12) dimethylnitrosoamine, (13) ketones, (14) *epi*chlorohydrin (*Zeitsch. physikal. Chem.*, 1906, **54**, 130). This system of classification will be adhered to in the following pages.

1. *Alcohols.*

(a) *Methyl Alcohol.*—One of the most trustworthy investigations on the conductivity of electrolytes in methyl-alcoholic solutions is that of Carrara (*Gazzetta*, 1896, **26**, i, 119). The observed values of μ_v in tables I and II are taken from his work. The dielectric constant of methyl alcohol at 20° is 32·5. At 25° it is somewhat less; in the calculations, D has been taken as equal to 31. The solutes in tables I and II are all binary electrolytes, and μ_∞ is obtained from any particular value of μ_v by applying the equation

$$\frac{N . E^2 \sqrt[3]{2N}}{D . \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This particular value of μ_∞ is afterwards utilised to calculate the molecular conductivity at other dilutions. It will be seen

from tables I and II that the agreement between the calculated and observed values of μ_v is very good, both in the case of the binary salts and the acids.

Carrara (*loc. cit.*) has also determined the molecular conductivities of strontium iodide in methyl alcohol at various dilutions. Here we expect the equation for ternary electrolytes:

$$\frac{3N \,.\, E^2 \,.\, 2 \,.\, \sqrt[3]{2N}}{D \,.\, \sqrt{3} \,.\, \sqrt[3]{V}} = 3RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad (2)$$

to hold good. Table III shows how well the calculated values agree with those observed.

TABLE I.

Solvent: Methyl alcohol. T=25°.

Solute.	μ_∞ calc. from μ_{128}	$v =$	32.	64.	128.	256.	512.
1. NaI......	94·0	μ_v calc.	68·9	73·5	77·3	80·5	83·0
		μ_v obs.	68·8	73·1	77·3	79·9	82·2
2. NaBr....	91·8	μ_v calc.	67·3	71·8	75·5	78·6	81·1
		μ_v obs.	65·8	71·0	75·5	79·9	82·8
3. NaCl ...	90·4	μ_v calc.	—	70·6	74·3	77·4	79·8
		μ_v obs.	—	69·6	74·3	78·1	81·8
4. KI	102·8	μ_v calc.	75·3	80·3	84·5	88·0	90·8
		μ_v obs.	73·8	79·5	84·5	88·5	91·0

TABLE II.

Solvent: Methyl alcohol. T=25°.

Solute.	μ_∞ calc. from	$v =$			
		$v =$	18·9	37·7.	150·9.
HCl...	$\mu_{37\cdot7} = 157\cdot0$	μ_v calc.	108·4	117·0	130·4
		μ_v obs.	106·4	117·0	128·0
		$v =$	6·7.	26·8.	107·4.
HBr...	μ_∞ calc. from $\mu_{26\cdot8} = 142\cdot0$	μ_v calc.	84·0	101·9	115·0
		μ_v obs.	88·0	101·9	113·1
		$v =$	17·9.	71·4.	245·7.
HI ...	μ_∞ calc. from $\mu_{71\cdot4} = 152\cdot2$	μ_v calc.	104·4	120·0	130·0
		μ_v obs.	104·6	120·0	130·5

TABLE III.

Solvent: Methyl alcohol. T=25°

Solute.	μ_∞ calc. from	$v =$	64.	128.	256.	512.
SrI_2...	$\mu_{128} = 200\cdot4$	μ_v calc.	114·6	128·6	141·0	151·2
		μ_v obs.	115·3	128·6	141·4	153·5

The most complete investigation in the field of non-aqueous solutions is that of Walden on solutions of tetraethylammonium iodide in various solvents. It is natural to expect that tetraethylammonium iodide would dissociate according to the following equation:

$$NEt_4I = NEt_4^{\cdot} + I'.$$

Except in the case of aldehydes, the variation of equivalent conductivity with dilution calculated from the equation for binary electrolytes (1) does not agree with the observed values. If, however, we assume that tetraethylammonium iodide at first undergoes polymerisation and then the double molecule $[NEt_4I]_2$ dissociates as a ternary electrolyte according to the equation:

$$[NEt_4I]_2 = 2NEt_4^{\cdot} + I_2'',$$

the calculated values of equivalent conductivities agree extremely well with the observed ones. Indeed, a cursory examination of the data on the variation of equivalent conductivity with dilution will at once lead to the conviction that the electrolytic dissociation of potassium iodide and tetraethylammonium iodide is not of the same type. If it were so, the variation of λ_v (equivalent conductivity) with dilution would have been of the same order. As a matter of fact, whilst λ_v for potassium iodide varies from 80·3 to 84·5 as the dilution increases from 64 to 128, the value for tetraethylammonium iodide increases by 8 units from 83·1 to 91·1 for the same change in dilution. Iodine has a great tendency to form complex ions. We are already acquainted with I_3', I_5' ions, etc. It is therefore not at all unreasonable to assume that in tetraethylammonium iodide solutions there exists a complex iodine ion of the type I_2''. Again, the consensus of opinion among electrochemists is generally in favour of complex molecules in non-aqueous solutions. The exact coincidence between the observed and calculated values of equivalent conductivity for tetraethylammonium iodide solutions, as shown in table IV, leaves no room for doubt as to the mode of dissociation of this salt in methylalcoholic solution. Of course, the above equation is equally applicable if the salt dissociates, thus:

$$[NEt_4I]_2 = [NEt_4]_2^{\cdot\cdot} + 2I'.$$

TABLE IV.

Solvent: Methyl alcohol. T = 25°.

Solute.	λ_∞ calc. from	$V' =$	64.	127.	256.	512.	1024.
NEt_4I...	$\lambda_{128} = 130$	λ_v calc.	83·1	91·1	97·7	104·0	108·9
		λ_v obs.	82·1	91·1	98·0	103·6	108·6

In the above table V′ is the equivalent dilution.

(*b*) *Ethyl Alcohol and Propyl Alcohol.*—The dielectric constant of ethyl alcohol at 20° is 21·7 (Walden, *loc. cit.*). In table V the observed values of molecular conductivity are taken from the work of Jones and Lindsay (*Amer. Chem. J.*, 1902, **28**, 341) (*loc. cit.*).

The conductivity of sodium iodide in propyl alcohol has been determined by Schlamp (*Zeitsch. physikal. Chem.*, 1894, **14**, 280). The dielectric constant of propyl alcohol, according to Rudolph, is 13·8.

TABLE V.

Solvent: Ethyl alcohol. T = 25°.

Solute.	μ_∞ calc. (equation 1) from	v =	64.	128.	256.	512.
KI.	$\mu_{256} = 44·9$	μ_v calc.	31·6	33·9	36·0	38·5
		μ_v obs.	29·6	33·0	36·0	38·5

TABLE VI.

Solvent: Propyl alcohol. T = 25°.

Solute.	μ_∞ calc. (equation 1) from	v =	19·8.	55·4.	166·3.	500.
NaI.	$\mu_{166·3} = 176·0$	μ_v calc.	79·0	99·5	118·7	135·0
		μ_v obs.	77·0	97·1	118·7	138·0

2. *Aldehydes.*

Acetaldehyde, Propaldehyde, and Furfuraldehyde.—The dielectric constant of acetaldehyde is 21·2, according to Walden, and 18·6 according to Thwing. It is quite probable that the great reactivity of the solvent and its tendency towards polmerisation will completely prevent the formation of complexes in the solute. It is therefore to be expected that here at least tetraethylammonium iodide will dissociate normally as a binary electrolyte. The dielectric constant of propaldehyde is 14, whilst that of furfuraldehyde is 39·4.

TABLE VII.

Solvent: Acetaldehyde. T = 0°.

Solute.	μ_∞ calc. (equation 1) from	v =	100.	1000.	4000.
NEt_4I.	$\mu_{1000} = 178$	μ_v calc.	124·0	151·0	160·0
		μ_v obs.	122·0	151·0	158·0

TABLE VIII.

Solvent: Propaldehyde. T=25°.

Solute.	μ_∞ calc. (equation 1) from	$v =$	100.	200.	400.	700.
NEt_4I.	$\mu_{200} = 127{\cdot}6$	μ_v calc.	81·0	89·0	95·8	101·8
		μ_v obs.	79·8	89·0	94·5	103·9

TABLE IX.

Solvent: Furfuraldehyde. T=25°.

Solute.	μ_∞ calc. (equation 1) from	$v =$	200.	400.	800.	1600.
NEt_4I.	$\mu_{400} = 47{\cdot}8$	μ_v calc.	42·2	43·4	44·3	45·0
		μ_v obs.	41·6	43·4	45·0	45·8

3. *Acids.*

TABLE X.

Solvent: Thioacetic acid. T=0°. D=17·3.

Solute.	λ_∞ calc. (equation 2) from	$V' =$	320.	640.	1280.
NEt_4I.	$\lambda_{640} = 52{\cdot}5$	λ_v calc.	33·2	36·6	39·5
		λ_v obs.	32·7	36·6	40·2

4. *Acid Anhydrides.*

The dielectric constant of citraconic anhydride is 39. The agreement in this case is perfect.

TABLE XI.

Solvent: Citraconic anhydride. T=25°.

Solute.	λ_∞ calc. (equation 2) from	$V' =$	100.	200.	400.	800.
NEt_4I	$\lambda_{200} = 24{\cdot}9$	λ_v calc.	18·5	19·7	20·7	21·5
		λ_v obs.	18·5	19·7	20·6	21·1

5. *Acid Chlorides and Bromides.*

In these solvents the agreement between the observed and calculated values of equivalent conductivity is always within the limits of experimental error, which is somewhat large.

6. *Esters.*

(*a*) *Organic Esters.*—The dielectric constant of methyl cyanoacetate is 28, and that of the ethyl ester is 26.

(*b*) *Inorganic Esters.*—Walden's data on the equivalent con-

ductivities of solutions of tetraethylammonium iodide in methyl sulphate, ethyl sulphate, and trimethyl borate are the most trustworthy. The dielectric constants are 46, 38, and 8 respectively. The agreement is always very good.

TABLE XII.

Solute: Tetraethylammonium iodide. T=25°.

Solvent.	λ_∞ calc. (equation 2) from	$V'=$	100.	200.	500.	1000.	2000.
Methyl cyano-acetate.	$\lambda_{500} = 30{\cdot}8$	λ_v calc.	20·4	22·2	24·2	25·3	26·4
		λ_v obs.	20·3	22·1	24·2	25·3	26·1
Ethyl cyano-acetate	$\lambda_{500} = 28{\cdot}1$	λ_v calc.	17·9	19·7	21·6	22·8	23·8
		λ_v obs.	17·7	19·6	21·6	22·8	23·6

TABLE XIII.

Solvent: Methyl sulphate. T=25°

Solute.	λ_∞ calc. (equation 2) from	$V'=$	200.	400.	800.	1600.	3200.
NEt_4I.	$\lambda_{400} = 44{\cdot}3$	λ_v calc.	36·1	37·7	38·9	39·9	40·7
		λ_v obs.	35·5	37·7	38·7	39·6	40·4

TABLE XIV.

Solvent: Ethyl sulphate. T=25°.

Solute.	λ_∞ calc. (equation 2) from	$V'=$	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 40{\cdot}5$	λ_v calc.	31·9	33·5	34·9	36·0
		λ_v obs.	30·3	33·5	35·6	36·7

TABLE XV.

Solvent: Trimethyl borate. T=25°.

Solute.	λ_∞ calc. (equation 2) from	$V'=$	200.	400.	800.
NEt_4I.	$\lambda_{400} = 32{\cdot}5$	λ_v calc.	10·2	13·0	15·7
		λ_v obs.	10·2	13·0	16·5

7. *Amides, Amines, etc.*

Among amides, formamide is a solvent that most resembles water. The inorganic salts dissolve in it quite as readily as in water, and, like the latter, it has a high dielectric constant, namely, 84.

Pyridine.—Laszczynski and Gorski have determined the conductivity of potassium iodide in pyridine solutions (*Zeitsch. Elektro-*

chem., 1897, **4**, 290), whilst Walden has determined the equivalent conductivity of tetraethylammonium iodide at various dilutions (*Zeitsch. physikal. Chem.*, 1906, **55**, 334). Acording to Schlundt, the dielectric constant of pyridine is 12·4 (*J. Physical Chem.*, 1901, **5**, 157, 503).

TABLE XVI.

Solvent: Formamide. T=25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	100.	200.	400.	800.
NEt_4I.	$\lambda_{200} = 29·0$	λ_v calc.	25·2	26·0	26·5	27·0
		λ_v obs.	25·0	26·0	26·6	27·2

TABLE XVII.

Solvent: Pyridine. T=25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	100.	200.	400.	800.
NEt_4I.	$\lambda_{400} = 71·0$	λ_v calc.	26·9	32·9	39·5	43·7
		λ_v obs.	27·0	33·0	39·5	46·0

	λ_∞ calc. (equation 2) from	V' =	178·5.	357·0.	714·0.
KI.	$\lambda_{714} = 50·0$	λ_v calc.	22·8	26·9	30·7
		λ_v obs.	22·0	26·2	30·7

8. *Nitriles.*

The nitriles are excellent ionisers, and their dielectric constants are high. Thus glycollonitrile has a dielectric constant as high as 68, whilst the dielectric constants of acetonitrile, propionitrile, and benzonitrile are 37, 27, and 26 respectively.

TABLE XVIII.

Solvent: Acetonitrile. T=25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	200.	500.	1000.	2000.	4000.	8000.
NaI.	$\lambda_{500}=199·3$	λ_v calc.	155·0	165·9	172·3	177·4	182·0	185·4
		λ_v obs.	151·0	165·9	171·0	176·7	181·0	183·5

TABLE XIX.

Solvent: Propionitrile. T=25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	64.	128.	256.	512.	1024.
NEt_4I.	$\lambda_{128} = 169$	λ_v calc.	102·6	113·7	123·5	131·6	138·6
		λ_v obs.	102·0	113·7	123·4	131·5	139·4

Table XX.

Solvent: Benzonitrile. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	$V' =$	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 55{\cdot}6$	λ_v calc.	39·0	42·0	44·5	46·6
		λ_v obs.	37·7	42·0	45·0	47·6

Table XXI.

Solvent: Glycollonitrile. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	$V' =$	100.	200.	800.
NEt_4I.	$\lambda_{200} = 79{\cdot}5$	λ_v calc.	67·0	69·4	73·0
		λ_v obs.	66·8	69·4	71·0

Table XXII.

Solvent: Acetonitrile. T = 25°.

Solute.	μ_∞ calc. (equation 2) from	$v =$	100.	200.	400.
$CuBr_2$	$\mu_{200} = 73{\cdot}9$	μ_v calc.	49·8	54·0	57·7
		μ_v obs.	48·6	54·0	58·0

9, 10. *Thiocyanates and Thiocarbimides.*

The calculated values of equivalent conductivity also agree well with Walden's data for these solvents.

11, 12. *Nitro-compounds and Dimethylnitrosoamine.*

The dielectric constants of nitromethane and dimethylnitrosoamine are 39 and 53·3 respectively.

Table XXIII.

Solvent: Nitromethane. T = 25°.

Solute.	λ_∞ calc. (equation 2) from.	$V' =$	100.	200.	400.	800.	1600.
NEt_4I.	$\lambda_{200} = 127{\cdot}8$	λ_v calc.	94·5	100·5	105·4	109·6	113·0
		λ_v obs.	94·0	100·5	105·9	109·5	112·0

Table XXIV.

Solvent: Dimethylnitrosoamine. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	$V' =$	250.	500.	1000.	2000.
NEt_4I.	$\lambda_{500} = 92{\cdot}0$	λ_v calc.	78·3	81·2	83·2	85·0
		λ_v obs.	77·5	81·2	84·2	86·4

13. *Ketones.*

The dielectric constant of acetone is 21, and that of acetylacetone is 22 at 25°.

TABLE XXV.

Solvent: Acetone. T=25°.

Solute.	μ_∞ calc. (equation 1) from	$v =$	256.	512.	1024.
NaI	$\mu_{512} = 158{\cdot}5$	μ_v calc.	127·0	133·0	138·0
		μ_v obs.	126·3	133·0	139·0

TABLE XXVI.

Solvent: Acetylacetone. T=25°.

Solute.	λ_∞ calc. (equation 2) from	$V' =$	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 86{\cdot}4$	λ_v calc.	56·9	62·0	66·4	70·0
		λ_v obs.	56·7	62·0	65·5	68·7

14. *Epichlorohydrin.*

TABLE XXVII.

Solvent: *epi*Chlorohydrin. T=25°. D=26.

Solute.	λ_∞ calc. (equation 2) from	$V' =$	100.	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 65{\cdot}7$	λ_v calc.	42·1	46·0	49·6	52·6	55·1
		λ_v obs.	40·0	45·0	49·6	53·7	56·8

Conclusion.

It will be seen that equations 1 and 2 have been subjected to a very severe test, and that their validity has been completely confirmed by the mass of experimental data on the conductivity of salt solutions in some thirty solvents.

The term "degree of dissociation" thus loses all significance in the case of strong electrolytes. In his first paper on the conduction of electricity by electrolytes, Arrhenius (*Bihang. der. Stockholmer. Akad.*, 1883, **8**, Nos. 13, 14) used the term "activity coefficient" for the ratio μ_v/μ_∞, and this is, indeed, a very suitable term in view of the fact successfully demonstrated here, that in salt solutions there are only free and bound ions. Incidentally, there has also been obtained a valuable method of determining the mode of dissociation of a solute in any solvent. Walden's normal electrolyte, tetraethylammonium iodide, really dissociates

abnormally. It is, however, the peculiar characteristic of this solute that the same type of dissociation persists in all the solvents. To this property are due the many regularities that Walden observed in tetraethylammonium iodide solutions. Thus we have his empirical law that "if solutions of one and the same normal electrolyte, tetraethylammonium iodide, in various solvents have the same degree of dissociation (activity coefficient), then for all solvents, the product of the dielectric constant, and the cube root of the dilution of that solution has always a constant value. Thus $D\sqrt[3]{V}=D'\sqrt[3]{V'}$, etc. $=k$, where D, D', etc., are the dielectric constants of the solvents, and V, V', etc., are the respective dilutions at which the activity-coefficient of tetraethylammonium iodide is the same. The theoretical significance of this general empirical law is at once brought out by equation 2. Since the mode of dissociation of the salt is always the same, the equation:

$$\frac{3N \,.\, E^2 \,.\, 2 \,.\, \sqrt[3]{2N}}{D \,.\, \sqrt{3}\,\sqrt[3]{V}} = 3RT\log_e\frac{\mu_\infty}{\mu_v}$$

is applicable to its solution in all solvents. For the same value of μ_v/μ_∞ it is obvious that

$$D\sqrt[3]{V}=k,$$

whatever be the nature of the solvent.

It was rightly suggested by Nernst and Thomson that the dielectric constant is the fundamental property which determines the dissociating power of a solvent. Walden's investigations proved conclusively that a direct parallelism exists between the dissociating power and the dielectric constants of solvents. The idea, however, never passed beyond the qualitative stage. In this paper, in the author's opinion, it has been proved beyond doubt that the exact quantitative relation between the activity-coefficient and the dielectric constant is given by equations 1 and 2.

Finally, it should be pointed out that the fundamental problem to be solved in this connexion is the work necessary to separate the constituent ions of a gram-molecule of a salt to an infinite distance at a given dilution. The assumption that the ions of a binary electrolyte are arranged according to a simple cubic lattice is necessarily arbitrary, although it is the simplest possible view. Some other views are possible, for example, we may have a face-centred cube lattice, a cube-centred lattice, etc. For ternary electrolytes good results have been obtained by assuming an arrangement corresponding with a fluorspar lattice. Here, also, it is possible that an ion, instead of occupying the centre of a cube, may be displaced diagonally towards an oppositely charged ion or towards an empty corner. Bragg has actually observed such dis-

placement in crystals of iron pyrites. It is therefore not necessary that the above rigid forms of equation should always be applicable. It ought to be always possible, however, to express the relation between the activity-coefficient, the dilution, and the dielectric constant of the solvent by equations of the above type. The behaviour of acetone solutions of ammonium iodide is a case in point. Equation 2 does not hold good in this case. If, however, we assume that the $NH_4^{\cdot}$ ions are displaced diagonally towards the oppositely charged I_2'' ion by one-fourth the length of the diagonal we get the following equation:

$$\frac{3N \,.\, E^2 \,.\, 4\sqrt[3]{2N}}{D \,.\, \sqrt{3} \,.\, \sqrt[3]{V}} = 3RT \log_e \frac{\mu_\infty}{\mu_v}.$$

which holds good exactly as shown in table XXVIII.

TABLE XXVIII.

Solvent: Acetone.

Solute.	λ_∞ calc. from		$V' =$	128.	256.	512.	1024.	2048.
NH_4I.	$\lambda_{512} = 209$	......	λ_v calc.	69·0	86·9	104·1	120·2	135·0
			λ_v obs.	67·5	85·5	104·1	120·8	136·0

The above theory should not, therefore, be rejected in those cases where equations 1 and 2 do not hold good. We should rather proceed in the reverse direction, that is, calculate the total potential energy of the electrical doublets at a given dilution, from the observed value of the activity-coefficient at that dilution. An insight into the arrangement of ions in the interior of a solution will then be easily obtained, and the next problem will be to determine whether the equation based on this particular arrangement holds good at other dilutions. Theory demands that such should be the case, and it fails if the observed and the calculated activity-coefficients do not agree. In some cases, however, chemical action may interfere, as in the hydrolysis of salts, and these should be regarded as abnormal.

The fundamental hypothesis that only ions exist in salt solutions requires no elaborate justification in view of the fact conclusively established that even in a salt crystal there is no such thing as a molecule.

My best thanks are due to Prof. P. C. Rây, and to my friend and colleague, Mr. J. N. Mukherjee.

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[*Received, October 2nd,* 1917.]

LIV.—*A New Synthesis of Tetraphenylpyrrole.*

By Gertrude Maud Robinson and Robert Robinson.

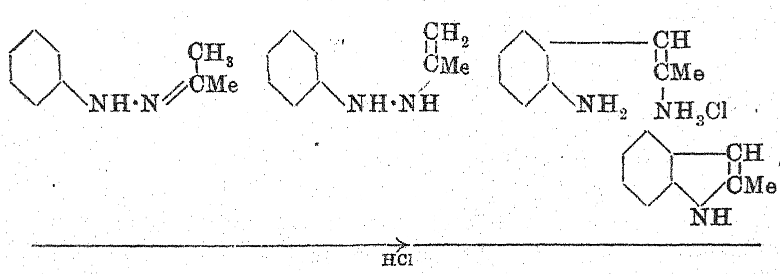
In the course of an investigation having for its object the preparation of pyrrole, as a starting point for tropine, by an improved method, our attention was naturally directed to known methods of producing the pyrrole nucleus, among which E. Fischer's well-known synthesis of indole derivatives (*Annalen*, 1886, **236**, 126) occupies a prominent position. A necessary preliminary, however, to an attempt to apply an analogous process to the formation of true pyrroles seemed to be the formulation of a clear idea of the mechanism of the reactions involved in the decomposition of phenylhydrazones, and we have adopted a hypothesis which includes the following three stages:

(1) The transformation of the hydrazone into an unsaturated hydrazine, which is the isomeric change of an enimic into an enamic modification (compare J. F. Thorpe, P., 1909, **25**, 309). This is assumed to occur by the addition of the acid reagent and decomposition of the additive product.

(2) The benzidine-type rearrangement of the resulting hydrazine.

(3) Ring-formation by elimination of ammonium salt from the product, analogous to the formation of piperidine from the hydrochloride of pentamethylenediamine.

These changes are represented below in the case of the synthesis of 2-methylindole from the phenylhydrazone of acetone.



It will at once be recognised that the conditions necessary for the reaction, namely, an acid reagent and an elevated temperature, are those which would be expected to favour each of the above stages if considered separately, and in accordance with experience of molecular transformations due to the intervention of an acidic reagent it is noted that each stage is more basic than the last until, finally, the basic character is neutralised by the accident of

the formation of a ring of benzenoid character.* Thus a hydrazine is more basic than a hydrazone, and the hypothetical diamino-compound should be more basic still.

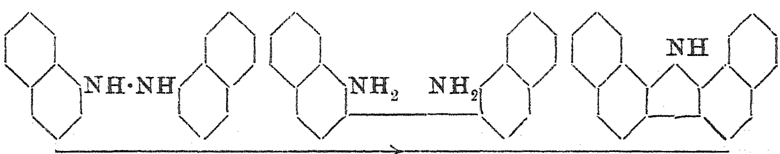
It seems probable that there is analogy between the enimic to enamic transformation and the ketone to enol change, and that the former would be likely to occur more easily in the cases of the hydrazones of those ketones which are readily changed to enols or enolic derivatives. The aldehydes and ketones, which are readily changed to enols, might therefore be expected to give phenylhydrazones readily convertible to indole derivatives if our hypothesis can be upheld. This is in accordance with experimental results, as the following examples show. Semmler (*Ber.*, 1909, **42**, 584) found that phenylacetaldehyde was converted into the acetate of the enolic modification by boiling with acetic anhydride, whereas acetophenone shows no such behaviour. Now Fischer and Schmitt (*Ber.*, 1888, **21**, 1072) showed that phenylacetaldehyde-phenylhydrazone was extremely easily transformed to phenylindole, and even by boiling with an alcoholic solution containing one-fifth of a molecular proportion of hydrochloric acid. On the other hand, acetophenonephenylhydrazone required heating with zinc chloride at 180° (Fischer, *loc. cit.*, p. 133). A similar comparison may be made between the cyclic ketones, such as *cyclo*hexanone and corresponding open-chain ketones. The former are well known to be more reactive than the latter in reactions which are assumed to depend on the enolic modification of the substances, and again the phenylhydrazones of the cyclic ketones are more readily transformed into indole derivatives than is the case with the phenylhydrazones of such ketones as diethyl ketone (compare Baeyer, *Annalen*, 1893, **278**, 106; Plancher, *Gazzetta*, 1898, **28**, ii, 387; Mannich, *Ber.*, 1906, **39**, 1594). In general, indoles appear to be readily produced from the phenylhydrazones of aldehydes and ketones which contain a negative group, particularly when this is in the β-position with respect to the carbonyl group.

It is interesting that Nef (*Annalen*, 1891, **266**, 71) observed the production of an indole derivative by dissolving ethyl β-phenylhydrazinocrotonate in concentrated sulphuric acid. This condensation product of phenylhydrazine and ethyl acetoacetate has

* The complete cyclic conjugation, which is probably the most characteristic feature of systems recognised as benzenoid, demands in the case of pyrrole a call on the latent valencies of the nitrogen atom. In pyridine, however, the latent valencies remain unaltered. It is possible, therefore, that a salt of pyridine retains its aromatic nucleus, whereas a salt of pyrrole cannot do so. Further, the latent valencies in pyrrole having been weakened, the preliminary dissociation necessary before salt-formation can take place is less likely to occur.

undoubtedly the unsaturated hydrazine structure, since it may be oxidised by mercuric oxide to an azo-compound previously obtained by Bender (*Ber.*, 1887, **26**, 2747), but under most conditions of condensation it merely loses alcohol with the formation of phenylmethylpyrazolone.

In the second phase of the reaction, an ortho-benzidine-type re-arrangement has been assumed, and this may be realised in the case of certain naphthalene derivatives. Thus Nietzki and Goll (*Ber.*, 1885, **18**, 3252) obtained the isomeric diaminodinaphthyls, naphthidine and dinaphthyline, by the action of stannous chloride and hydrochloric acid on α-azonaphthalene, and, further, obtained a dinaphthacarbazole by boiling dinaphthyline with concentrated hydrochloric acid. Vesely (*Ber.*, 1905, **38**, 136) determined the constitution of the dinaphthacarbazole by an independent synthesis, so that the following changes are established:



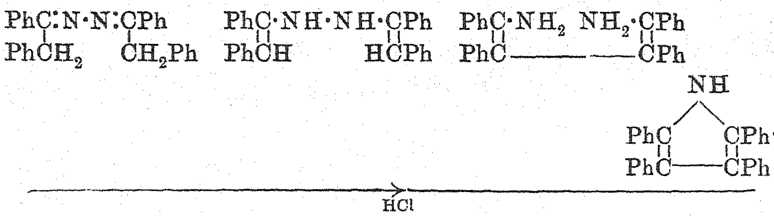
HCl

The similar formation of a dinaphthacarbazole from β-hydrazonaphthalene has been described by Meisenheimer and Witte (*Ber.*, 1903, **36**, 4161), and in these reactions we may perceive precise analogies to the second and the third stages of the synthesis of indoles from phenylhydrazones as postulated above.

Attention may also be directed to an interesting paper by Japp and Maitland (T., 1903, **83**, 267), who obtained carbazoles by heating phenols, such as β-naphthol, with arylhydrazines and their salts. These authors thought it probable that the phenol reacted in its tautomeric keto-modification with the production of a hydrazone, but even if this is the case, we are of the opinion that the next stage would be conversion to the hydrazine, bringing this part of the process into line with the formation of naphthylamine from naphthol by the action of ammonia, followed by reactions entirely similar to those involved in the two examples from the naphthalene series which are quoted above. The formation of a small quantity of *as*-1:2-dinaphthazine was observed by Japp and Maitland on heating β-naphthol with β-naphthylhydrazine and its hydrochloride. This could be explained as the result of a semidine transformation of β-hydrazonaphthalene followed by oxidation.

The application of the foregoing to the question of the possibility of synthesis of pyrrole derivatives by a corresponding method

seemed to be that divinylhydrazine and its derivatives should be convertible by acids into pyrrole and substituted pyrroles. Continuing this line of argument and reasoning from the first stage assumed above, it appeared not improbable that azines of substances containing the group $\cdot CH_2\cdot CO\cdot$ might also, under correct conditions, be transformed into pyrroles. In this case, the initial tautomeric change is a double one and only likely to occur with facility in the molecules of azines of those ketones or aldehydes which show a marked tendency to change to related enols. To test our hypothesis, we chose what was regarded as one of the more favourable cases, namely, that of the azine of deoxybenzoin, and found that the action of dry hydrogen chloride on this substance at 180° converted it in almost a quantitative manner into the expected tetraphenylpyrrole and ammonium chloride. The reactions involved are represented below, in accordance with the views already discussed.



The scope of the reaction has not yet been defined, but in the case of the simpler aliphatic azines there is the competing transformation to pyrazolines, and we have been unable to obtain pyrrole from acetaldazine or dimethylpyrrole from dimethyl ketazine. The above explanation assumes what is perhaps a somewhat wider view of the benzidine transformation than is generally held, and in this connexion we have found the theory of partial dissociations serviceable.

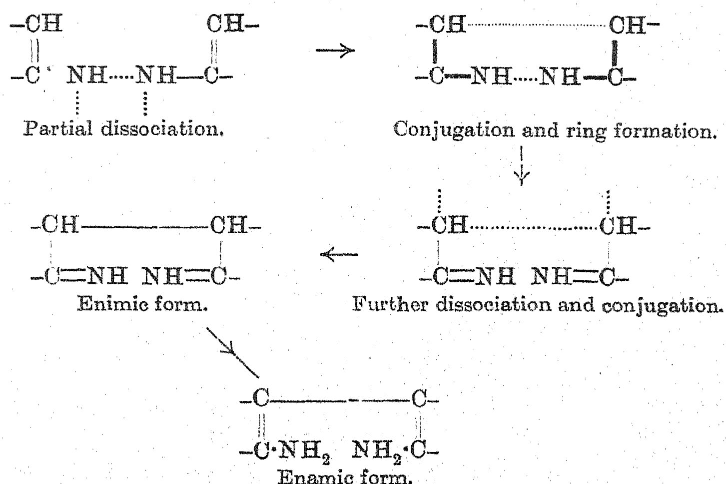
The following brief statement expresses the form in which this and related reactions may be generalised. In a molecular complex $A—b—c—D$, b or c or both represent atoms capable of assuming a higher valency by salt-formation. The salt absorbs energy and passes into an activated condition,* represented by $A—b\cdots c—D$

* The activated molecules are said to be 'partially dissociated' because the phenomenon appears to be a stage towards complete ionic dissociation, but the physical basis of the process is not quite clear. It may be that the energy change causes the movement of an electron from one atom to another (polarisation of the molecule) or a mere change in the position of one or more electrons within the sphere of the atom itself. In this case the evidence shows that the change is repeated in the same sense in alternate atoms

omitting the acid for reasons of convenience. If the partial valencies become conjugated with unsaturated groups in *A* or *D*, we obtain

$$A—b\cdots c—D \qquad \text{and} \qquad A—b\cdots c—D\,.$$

Ring-formation by the partial valencies followed by a second similar complete process leads in the first case to *b*—*A*—*c*—*D* and in the second to *b*—*A*—*D*—*c*. The products are obtained in the *keto*-, *enimic*, or *thioketo*-modifications, according as the atoms *b* or *c* are oxygen, nitrogen, or sulphur. The less extensive change is represented by the semidine transformation, the conversion of phenylhydrazine into *p*-phenylenediamine, of phenylnitroamine into nitroaniline, and by many other reactions. The full change resulting from conjugation of the partial valencies with both unsaturated groups *A* and *D* is represented by the benzidine rearrangement, and it is obvious that even within the four corners of the general scheme the nature of the products may be considerably varied according as the conjugated chains in *A* and *D* are long or short. The type of rearrangement assumed to occur in the synthesis of indole derivatives is represented below, and the thickened lines stand for a normal valency plus a partial valency.



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forming part of a conjugated chain and in the opposite sense in the other atoms of the chain. Several further suggestions might be made, especially that a part use may be made of the field surrounding a single electron.

EXPERIMENTAL.

Preparation of Azines.

The processes described in the literature for the preparation of azines, and especially the ketazines, are far from convenient, and the employment of free hydrazine does not, in our experience, give such good results as that of a hydrazine salt and sodium acetate. The ketazines are readily obtained by the interaction of the calculated amounts of ketone and hydrazine sulphate in boiling aqueous alcohol in the presence of excess of sodium acetate. The yields correspond closely with those demanded by theory.

Phenyl benzyl ketazine was prepared by boiling a mixture of deoxybenzoin (6·3 grams), hydrazine sulphate (2·2 grams), sodium acetate (7 grams), water (60 c.c.), and alcohol (125 c.c.) during two hours under reflux. The product was collected and crystallised from ethyl acetate, and then melted at 164°, as stated by Curtius and Blumer (*J. pr. Chem.*, 1895, [ii], **52**, 137). This azine is quickly and completely hydrolysed by heating for a minute with alcohol and hydrochloric acid, and on the addition of water pure deoxybenzoin is precipitated. In view of the sparing solubility of the derivative, it may advantageously be employed for the otherwise rather troublesome purification of crude deoxybenzoin.

Tetraphenylpyrrole.

Evidence of the formation of tetraphenylpyrrole was obtained when phenyl benzyl ketazine was heated with zinc chloride, but the yield is much improved when dry hydrogen chloride is passed over the melted substance contained in a vessel heated at 180° in an oil-bath. The reaction was prolonged during an hour, and the solid product was found to consist of a mixture of ammonium chloride and the pyrrole derivative. The mass was extracted with sufficient hot acetic acid, and the crystals which separated on cooling were collected and washed with a little water to remove traces of ammonium salt. The yield of crude, dry tetraphenylpyrrole amounted to 88 per cent. of the theoretical. The substance was recrystallised several times from acetic acid, and obtained in colourless, flat needles melting at 214—215°. A specimen was prepared according to Garrett's method (*Ber.*, 1888, **21**, 3107), and found to melt at 214—215°, and a mixture of the two also melted at the same temperature.

The yellow solution in sulphuric acid becomes ivy-green on the addition of a trace of a nitrite or of a drop of nitric acid. In the

latter case, however, the liquid soon becomes brown, and on the addition of water a yellow nitro-derivative is precipitated. Acetaldazine and dimethyl ketazine were submitted to the action of dry hydrogen chloride, sulphanilic acid, and a number of other acid reagents and salts, such as zinc chloride, under varied conditions, but in all cases no pyrrole derivative was obtained, the only products being the corresponding pyrazoles and pyrazolines.

The formation of benzidine from hydrazobenzene has been discussed above, and a theory which has been occasionally advocated regards the transformation as passing through the intermediate stage of *p*-aminodiphenylamine. The method of preparation of this substance indicates its stability under conditions which favour the transformation of hydrazobenzene into benzidine, but to be more sure we prepared the compound by the usual process and endeavoured to convert it into benzidine, but without success. It was entirely unaffected by boiling with dilute or concentrated hydrochloric acid. 0·9 Gram of aminodiphenylamine was boiled during thirty minutes with 15 c.c. of concentrated hydrochloric acid; 0·82 gram of unaltered substance melting, after crystallisation from light petroleum, at 66—67° was recovered.

UNIVERSITY OF LIVERPOOL. [*Received, July 18th, 1918.*]

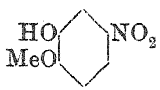
LV.—*Nitro-derivatives of Guaiacol.*

By FANNY POLLECOFF and ROBERT ROBINSON.

THE opinion has been expressed (Jones and Robinson, T., 1917, **111**, 906 *) that negative groups in the meta-position with respect

* In this paper the melting point of 6-bromoacetoveratrylamide was wrongly given owing to a clerical error (*loc. cit.*, p. 913). The melting point of this substance is 127°. In the same communication 6-nitroacetoveratrylamide melting at 199° and 6-nitroveratrylamine melting at 175° were described. Simonsen and Rau (this vol., p. 28) prepared the same substances and assigned to them the respective melting points 196° and 171°. A redetermination of the melting points of the specimens which had been preserved gave 199° for the acetyl derivative, whilst 6-nitroveratrylamine melted at 174·5°. The latter crystallises both in needles and in prisms. It is possible that the discrepancy is due to the fact that Jones and Robinson nitrated acetoveratrylamide in acetic acid solution, whilst Simonsen and Rau employed more concentrated nitric acid (D 1·4). Simonsen and Rau (*loc. cit.*) experienced difficulty in preparing veratrylamine unmixed with its chloro-derivative by the reduction of nitroveratrole with tin and hydrochloric acid, but were finally able to obtain a 50 per cent. yield by reducing at 100° with tin and hydrochloric acid in presence of graphite. We found that an

to a positive group exert an influence which is in the direction of favouring ortho-substitution with respect to the positive orientator. An example was found in the bromination of 5-nitroguaiacol (I), which yielded 6-bromo-5-nitroguaiacol (II), and we have now investigated the nitration of the same substance, and find that the main product is 5:6-dinitroguaiacol (III), mixed, however, with no inconsiderable proportion of 4:5-dinitroguaiacol (IV).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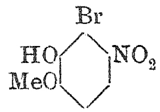
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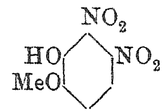
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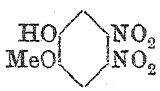
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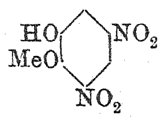
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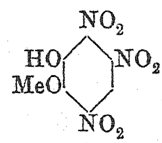
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It was obviously interesting to extend the inquiry to the nitration of 3:5-dinitroguaiacol (V), in which there are two negative groups in the meta-position with respect to the phenolic hydroxyl. The desired substance was obtained by the nitration of guaiacol carbonate, which was changed first to a dinitro-derivative, the carbonate of 5-nitroguaiacol, and then to a tetranitro-derivative, which on hydrolysis yielded the new 3:5-dinitroguaiacol.

As was anticipated, the nitration of the latter resulted in 3:5:6-trinitroguaiacol (VI) as the sole product. The necessary proofs of constitution are obtained from the observations that the dinitroguaiacol from the tetranitro-derivative of guaiacol carbonate yields 4:6-dinitroveratrole on methylation, and that the methyl ether of the trinitroguaiacol is a new trinitroveratrole melting at 174°. The melting points of the known nitroguaiacols are tabulated below, in order to bring out the striking divergences which exist:

4-Nitroguaiacol, 101—102°.
5-Nitroguaiacol, 105°
6-Nitroguaiacol, 62°.

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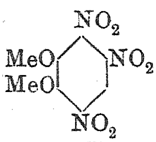
excellent yield could be obtained by shaking the nitroveratrole with tin, stannous chloride, hydrochloric acid, and some acetic acid in the cold until the reaction was complete. The amine was usually isolated as the acetyl derivative by eliminating the tin by the addition of zinc, and after rendering strongly alkaline with sodium hydroxide the solution was agitated with acetic anhydride. The crystalline precipitate of acetoveratrylamide was collected. Further quantities could be obtained by extraction of the alkaline solution with ether. R. R.

3-Nitroguaiacol is unknown.
3 : 5-Dinitroguaiacol, 80°.
3 : 5 : 6-Trinitroguaiacol, 129° (decomp.) 3 : 4 : 5-, 4 : 5 : 6-, and 3 : 4 : 6-trinitroguaiacols are unknown.
4 : 6-Dinitroguaiacol, 124°.
4 : 5-Dinitroguaiacol, 172°.
5 : 6-Dinitroguaiacol, 205—208° (decomp.).
3 : 5- and 3 : 4-Dinitroguaiacols are unknown.

3 : 5 : 6-Trinitroveratrole (VII) is changed by aqueous methyl-alcoholic ammonia into 3 : 5-dinitro-2 : 6-diaminoanisole (VIII), and by methyl-alcoholic sodium hydroxide into 4 : 6-dinitro-1 : 2 : 3-trimethoxybenzene (IX). The nitro-group displaced by ammonia is therefore that which is also displaceable by methoxyl, and in this respect the substance differs from the isomeric 3 : 4 : 5-trinitroveratrole, in which the nitro-group in position 4 is affected by ammonia, whilst that in position 5 is displaced by methoxyl when the trinitroveratrole is heated with a solution containing sodium methoxide.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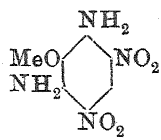
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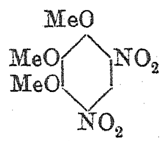

(IX.)

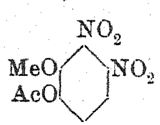
EXPERIMENTAL.

Preparation of 4-Nitroguaiacol.

Cardwell and Robinson (T., 1915, **107**, 255) prepared this substance by the hydrolysis of nitroveratrole by means of boiling aqueous methyl-alcoholic potassium hydroxide, but the yield was not quite satisfactory, and a certain amount of neutral material was recovered. It is now found that this consists partly of azoxyveratrole (compare G. M. Robinson, T., 1917, **111**, 109), and that if the methyl alcohol is omitted, the hydrolysis, although slow, proceeds practically quantitatively. The modified process constitutes by far the most convenient method available for the preparation of 4-nitroguaiacol. Nitroveratrole (5 grams) was boiled during thirty-six hours with a 10 per cent. aqueous solution (100 grams) of potassium hydroxide under reflux, and, on cooling, the potassium salt of the nitroguaiacol crystallised in golden-orange needles. Sufficient water to dissolve the salt was added, and on the addition of hydrochloric acid, 4-nitroguaiacol was precipitated in the crystalline condition, and was collected and dried in the air.

Nitration of 4-Nitroguaiacol and its Acetyl Derivative.

4-Nitroguaiacol was dissolved in nitric acid (D 1·42), when immediate reaction ensued, and, on the addition of water, a mass of needle-shaped crystals of 4:6-dinitroguaiacol was precipitated. The substance melted at 123° after crystallisation from alcohol, and gave a methyl ether melting after crystallisation at 101—102°. The yield closely approximated to that demanded by theory. 4-Nitroguaiacyl acetate is not affected by cold nitric acid (D 1·42), and although it is attacked by the fuming acid (D 1·5), the experiment is rather unsatisfactory, owing to the considerable loss which occurs through oxidation. The acetyl derivative was dissolved in ten times its weight of nitric acid (D 1·5), and the mixture cooled in running water at 15° during fifteen minutes. The product was poured into water, when the oil soon solidified, and after collection, washing, and drying, weighed approximately half as much as the material employed. Repeated crystallisations from methyl alcohol resulted in the isolation of unchanged 4-nitroguaiacyl acetate, but, after hydrolysing the acetyl derivatives contained in the mother liquors by the addition of dilute aqueous potassium hydroxide and gently heating the solution, a precipitate of 4:5-dinitroguaiacol (see below) was obtained on acidification. When the nitration was carried out during only two minutes, much unchanged material was recovered, and the methyl-alcoholic mother liquors were in this case treated with potassium hydroxide and methyl sulphate in large excess; the resulting methyl ethers on repeated crystallisation from methyl alcohol yielded pure 3:4-dinitroveratrole melting at 91°. The nitration of 4-nitroguaiacyl acetate, therefore, results in the production of the compounds



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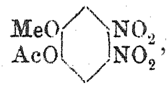
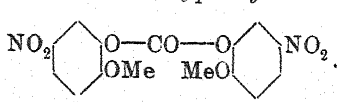


in undetermined proportions, and the loss on continued nitration appears to be due to the destruction of the first of these by oxidation.

5-Nitro-2-methoxyphenyl Carbonate,



Guaiacol carbonate (10 grams) was finely powdered and added in one portion to nitric acid (100 c.c., D 1·42), mechanically stirred,

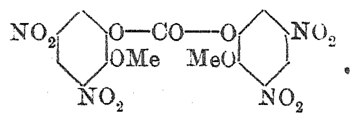
and cooled to 0°. These conditions were maintained during three hours; water was then added, and the nearly colourless product collected and well washed with water. The yield is excellent and the material sufficiently pure for further experiments, especially if it be extracted with a little warm alcohol. The substance crystallises from methyl alcohol in colourless needles melting at 133°, and moderately sparingly soluble in the usual solvents:

0·1663 gave 0·2999 CO_2 and 0·0510 H_2O. C=49·2; H=3·4.

$C_{15}H_{12}O_9N_2$ requires C=49·5; H=3·3 per cent.

The substance yields 5-nitroguaiacol on hydrolysis, and is a convenient source of the latter. The carbonate (4 grams) was heated on the steam-bath with a solution of sodium hydroxide (3 grams) in water (60 c.c.) until a clear solution was obtained on dilution with water. On acidification with hydrochloric acid, pure 5-nitroguaiacol was obtained in needles.

3:5-*Dinitro-2-methoxyphenyl Carbonate*,



The foregoing carbonate of 5-nitroguaiacol (3 grams) was dissolved in nitric acid (20 c.c., D 1·5), and the solution allowed to remain at the ordinary temperature during four hours. A certain proportion of the tetranitro-derivative separated in needles and the remainder was precipitated on the addition of water. The yield was almost that demanded by theory. The substance separated from benzene in short, colourless needles melting at 148°:

0·2113 gave 0·3050 CO_2 and 0·0403 H_2O. C=39·4; H=2·1.

$C_{15}H_{10}O_{13}N_4$ requires C=39·6; H=2·2 per cent.

This compound is readily soluble in ethyl acetate, sparingly so in ether or alcohol, and moderately so in benzene. There was no evidence of the formation of isomeric nitro-derivatives in the two stages of the nitration of guaiacol carbonate.

3:5-*Dinitroguaiacol* (V).

The carbonate (20 grams) described in the last section was heated on the steam-bath with sodium carbonate (50 c.c. of saturated aqueous solution), water (100 c.c.), and alcohol (30 c.c.) until a homogeneous solution resulted. After cooling, the nitrophenol was precipitated by the addition of hydrochloric acid, collected, washed

with water, and dried (18·5 grams). The substance was readily soluble in alcohol or ethyl acetate, more sparingly so in benzene, chloroform, or carbon disulphide. It was crystallised from toluene and then from carbon disulphide, and obtained in pale yellow needles melting at 80°:

0·2948 gave 0·4203 CO_2 and 0·0699 H_2O. C=39·0; H=2·6.

$C_7H_6O_6N_2$ requires C=39·2; H=2·8 per cent.

This dinitroguaiacol dissolves readily in aqueous sodium carbonate to a yellow solution, and the sodium salt is obtained in glistening, orange needles by the addition of sodium hydroxide. Not containing a nitro-group in the ortho- or para-position with respect to the hydroxyl group, this substance may be comparatively readily methylated in alcoholic solution by means of methyl sulphate and potassium hydroxide, but even in this case it was found more convenient to employ the xylene–methyl sulphate–sodium carbonate method. The methyl ether was identified with 3:5-(or 4:6-)-dinitroveratrole, melting after crystallisation from alcohol at 102°.

5:6-*Dinitroguaiacol* (III).

5-Nitroguaiacol (15 grams) in acetic acid (50 c.c.) was nitrated by the addition of nitric acid (20 c.c., D 1·42), diluted with acetic acid (10 c.c.) with constant stirring, and cooling in running water. The first half of the acid mixture was added during five minutes and the second portion during one minute. Water was then added immediately, and the product collected, washed, and dried (14·7 grams). This was dissolved in hot ethyl acetate (65 c.c.), and, on cooling, 4·8 grams of well-defined yellow prisms were deposited. The mother liquor was mixed with an equal volume of benzene, and this induced no further separation, but, on the addition of 100 c.c. of light petroleum, 2·5 grams gradually crystallised. This material was a mixture, and by further treatment with ethyl acetate and light petroleum ultimately yielded 2·2 grams of the yellow prisms. A further 0·1 gram was obtained from the mother liquors after separation of the 4:5-isomeride (see below), so that the total yield was 7·1 grams. The substance so isolated was practically pure 5:6-dinitroguaiacol, and it was crystallised, first from ethyl acetate and then again from toluene, and obtained in pale yellow prisms which became orange at about 200° and began to melt at 205°, with vigorous decomposition near 208°:

0·1071 gave 0·1547 CO_2 and 0·0280 H_2O. C=39·4; H=2·9.

$C_7H_6O_6N_2$ requires C=39·2; H=2·8 per cent.

This substance is more sparingly soluble in most organic solvents

than any of the isomerides which we have examined. It dissolves in aqueous sodium carbonate, and, on the addition of concentrated sodium hydroxide, an orange salt is precipitated in shining needles.

The *acetyl* derivative is obtained by heating the nitrophenol with acetic anhydride, and crystallises from alcohol, in which it is somewhat sparingly soluble in the cold, in slender, pointed, colourless needles melting at 124—125°.

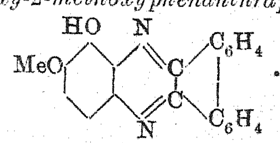
The *methyl ether* is identical with 3:4-dinitroveratrole, and was prepared by methylation with methyl sulphate and sodium carbonate in boiling xylene solution. The residue from the removal of the solvent in a current of steam was collected and crystallised many times from methyl alcohol, and obtained in flat needles melting at 91°:

0·1158 gave 0·1784 CO_2 and 0·0383 H_2O. C=42·0; H=3·7.

$C_8H_8O_6N_2$ requires C=42·1; H=3·5 per cent.

Jones and Robinson (T., 1917, **111**, 911) obtained a product melting at 96°, with previous softening, by the nitration of 3-nitroveratrole, and this was shown to contain 3:4-dinitroveratrole, because, after reduction and condensation with phenanthraquinone, 1:2-dimethoxyphenanthraphenazine (Pisovschi, *Ber.*, 1910, **43**, 2137) was obtained. It was pointed out at the time that the product was obviously impure, and it now appears that it must have contained 4:5-dinitroveratrole, owing to the presence of 4-nitroveratrole in the 3-nitroveratrole, which was the starting point, and we have therefore repeated the experiment with carefully purified 3-nitroveratrole, and have obtained a product melting at 91° and identical with that described above.

1-*Hydroxy*-2-*methoxyphenanthraphenazine*,



5:6-Dinitroguaiacol was reduced by the addition of zinc dust in excess to its solution in aqueous alcoholic hydrochloric acid, and the filtered solution, mixed with sodium acetate, was then heated with phenanthraquinone dissolved in hot aqueous sodium hydrogen sulphite. The precipitated phenazine derivative was collected and washed with alcohol, after which it was crystallised from acetic acid, and again by adding alcohol to its solution in nitrobenzene. It was obtained in glistening, golden-yellow needles melting at 224°, and dissolving in sulphuric acid to a rose-red solution:

0·0961 gave 0·2715 CO_2 and 0·0418 H_2O. C=77·5; H=4·7.
$C_{21}H_{14}O_2N_2$ requires C=77·3; H=4·3 per cent.

In alcoholic suspension, the substance was converted by sodium hydroxide into a dull mauve-red sodium salt, which reacted very readily with methyl sulphate with the production of 1:2-dimethoxyphenanthraphenazine (Pisovschi, *loc. cit.*), melting after crystallisation from alcohol at 175°. The curious colour of this sodium derivative appeared to be characteristic of the substance, and persists in the microscopic threads which separate from hot alcoholic solutions of the compound.

4:5-*Dinitroguaiacol* (IV).

The ethyl acetate–benzene–light petroleum mother liquor from the crystallisation of 5:6-dinitroguaiacol in the preparation described above (starting with 15 grams of 5-nitroguaiacol) was shaken with dilute sodium hydroxide, and the separated aqueous solution acidified with hydrochloric acid. The recovered nitrophenols were collected and found to consist chiefly of 4:5-dinitroguaiacol. The material was crystallised from a litre of boiling water, and obtained in long, yellow needles, and then again from toluene. The aqueous mother liquor was rendered alkaline and used to wash the toluene mother liquors, after which the solution was acidified and extracted with ether. The residue, after evaporation, was submitted to treatment with ethyl acetate, and, as already stated, some 5:6-dinitroguaiacol was isolated. Altogether, 5·7 grams of the 4:5-isomeride were obtained. The substance crystallised in long, pale yellow needles melting, when quite pure, at 172°, but many crystallisations are necessary in order to reach this value, and apparently pure material melted at 163—165°. The purest specimen was obtained by crystallisation from water followed by recrystallisation from alcohol and from xylene:

0·1439 gave 0·2045 CO_2 and 0·0350 H_2O. C=38·8; H=2·8.
$C_7H_6O_6N_2$ requires C=39·2; H=2·8 per cent.

The *acetyl* derivative crystallises from methyl alcohol in colourless, prismatic needles which sinter at 114° and melt at 123—124°. It is sparingly soluble in cold methyl alcohol.

The *methyl ether*, obtained in the usual way, was identified with 4:5-dinitroveratrole.

2-*Hydroxy*-3-*methoxyphenanthraphenazine* was obtained from 4:5-dinitroguaiacol in the manner described above for the preparation of an analogous substance from 5:6-dinitroguaiacol. It crystallised best from carbon disulphide in silky, yellow threads

melting at 239—240°, and dissolving in sulphuric acid to a rich magenta solution.

3:5:6-*Trinitroguaiacol* (VI).

It was not found practicable further to nitrate 4:6-, 5:6-, or 4:5-dinitroguaiacol, but the 3:5-isomeride was readily converted into a trinitroguaiacol. 3:5-Dinitroguaiacol (40 grams) was dissolved in nitric acid (200 c.c., D 1·42), and any rise of temperature was checked by cooling in running water. After half an hour, a certain amount of the product had crystallised from the solution, and water (300 c.c.) was added and as much salt as would dissolve in the solution. The precipitate was collected, washed with a little brine, and then with the minimum of dilute hydrochloric acid, and dried in the air (38 grams). The substance crystallised from benzene in needles containing solvent of crystallisation, and from chloroform in yellow prisms, which melt at 129° with vigorous decomposition, and evolution of much gas at a slightly higher temperature. This decomposition is not accompanied by charring, and is apparently a smooth process resulting in definite products. When the substance was heated quite gently in a test-tube, there was a mild explosion and the production of relatively much hydrocyanic acid was observed. In combustions, a low result was always obtained for carbon, but the composition of the substance is fixed by other experiments, which are described below. The substance dissolves in water to an intensely yellow solution resembling in appearance a solution of potassium chromate, and on the addition of hydrochloric acid the colour changes to that of a dilute solution of picric acid, and the substance crystallises in prisms. Silk and wool are dyed from aqueous solutions, the former in greenish-yellow and the latter in orange-yellow shades. The trinitroguaiacol also resembles picric acid in forming sparingly soluble salts with bases, and it may be employed as an alkaloidal precipitant.

Attempts were made to compare its molecular weight with that of picric acid by titration of both nitrophenols with a solution of a basic dye, with which each compound forms a sufficiently sparingly soluble salt. After a number of trials, it was found that Rhodamine 6G gave satisfactory results. The method was the following. The nitrophenol solution was mixed with salt and a solution * of Rhodamine 6G containing approximately 1 gram in 500 c.c. of water gradually added with constant stirring to ensure formation of the additive product and in order to avoid premature salting out of the dye. When the supernatant liquid appeared to

* It was unnecessary to ascertain the exact strength of the solution.

have a slight fluorescence, the end-point was near, but not reached until a filtered portion of the solution had a faint pink colour. The reason for this is that when the concentration of nitrophenol is low, the rhodamine salt appears to be just sufficiently soluble to exhibit fluorescence in solution. It was found best to make a rough experiment first, and to repeat it in order to obtain the exact result:

0·2386 Gram of picric acid dissolved in water and made up to 250 c.c.

25 c.c. with 20 grams of salt required 56·2 c.c. of Rhodamine 6G solution.

0·2255 Gram of trinitroguaiacol dissolved in water and made up to 250 c.c.

25 c.c. with 20 grams of salt required 59·9 c.c. of Rhodamine 6G solution.

Whence, assuming equivalence of picric acid and trinitroguaiacol in regard to rhodamine base, M.W. = 258.

$C_7H_5O_8N_3$ requires M.W. = 259.

Pyridine Salt.—This highly characteristic derivative separates in slender, canary-yellow needles when a drop of pyridine is added to a dilute aqueous solution of trinitroguaiacol. It crystallises from methyl alcohol in long, yellow needles melting at 194—195° when quickly heated, but if slowly heated, the melting point may be found as low as 180°, or more usually in the neighbourhood of 185°. This behaviour is due to the decomposition which accompanies the melting, and is apparently slow at 180°. As the substance is very readily prepared and purified, it was used to prove that 3:5:6-trinitroguaiacol is the only product of the nitration of 3:5-dinitroguaiacol, and in this case the specimens were always compared by simultaneous heating:

0·2257 gave 0·3549 CO_2 and 0·0561 H_2O. C = 42·9; H = 2·8.

$C_7H_5O_8N_3,C_5H_5N$ requires C = 42·8; H = 3·0 per cent.

This derivative was isolated from the mother liquors from the crystallisation of 3:5:6-trinitroguaiacol, and also from the original nitric acid solution from which the crude product was separated. It was useful as a means of isolating the trinitroguaiacol from aqueous solution, and could be employed directly for the preparation of the trinitroveratrole described below.

3:5:6-*Trinitroveratrole* (VII).

This ether was readily obtained by the methylation of trinitroguaiacol or its pyridine salt by means of methyl sulphate and

sodium carbonate in boiling xylene solution. Care was taken to ensure reaction between the phenol and sodium carbonate before raising the mixture to the boiling point, since, although the sodium salt is comparatively stable, the free trinitroguaiacol undergoes decomposition in boiling xylene solution. Also, hot aqueous sodium carbonate has some action on the trinitroveratrole, and the xylene solution is accordingly poured away from the excess of sodium carbonate after the reaction, and then submitted to distillation in a current of steam. The pale brown powder which remains in the flask when the solvent has been removed is collected and crystallised from acetic acid, and then from alcohol. The substance is obtained in very pale yellow needles melting at 174°, and sparingly soluble in alcohol, acetic acid, or chloroform, but readily so in ethyl acetate or acetone. The solution in the latter solvent is yellow, and becomes orange on the addition of a drop of ammonia:

0·1317 gave 0·1710 CO_2 and 0·0335 H_2O. C=35·4; H=2·8.

$C_8H_7O_8N_3$ requires C=35·1; H=2·6 per cent.

The substance is sensitive to alkalis, and is decomposed slowly by cold aqueous sodium hydroxide and by boiling aqueous sodium carbonate. It reacts with primary and secondary bases with elimination of a nitro-group, but the products were not closely examined. On boiling with a concentrated solution of sodium sulphite, the substance is attacked, and in this and other respects it exhibits greater reactivity than the isomeric 3:4:5-trinitroveratrole. On the addition of salt to the resulting yellow solution, a pale yellow substance separated in flat needles, and this material had the properties that would be associated with the expected product, namely, *sodium* 3:5-*dinitroveratrole*-6-*sulphonate*.

3:5-*Dinitro*-2:6-*diaminoanisole* (VIII).

This substance was readily prepared by boiling 3:5:6-trinitroveratrole with an excess of methyl-alcoholic aqueous ammonia under reflux for half an hour. The red product crystallised from the hot solution, and, after cooling, was collected and several times crystallised from ethyl acetate. It is obtained in garnet needles which soften at 225° and melt at 237°, and is sparingly soluble in most organic solvents. In general character it resembles the isomeride which is obtained from 3:4:5-trinitroveratrole:

0·0981 gave 0·1331 CO_2 and 0·0319 H_2O. C=37·0; H=3·6.

$C_7H_8O_5N_4$ requires C=36·8; H=3·5 per cent.

The substance is devoid of basic character, and on boiling with dilute aqueous sodium hydroxide, ammonia is evolved and a corre-

sponding nitrophenol obtained. On acidifying the solution, the latter is precipitated in orange-yellow, flat needles.

4:6-Dinitro-1:2:3-trimethoxybenzene (IX).

3:5:6-Trinitroveratrole yielded a bright orange-red solution on the addition of powdered potassium hydroxide to its suspension in methyl alcohol, and, on boiling, the colour gradually faded, and finally a yellow solution was obtained. On the addition of water, an oil separated, and after a short time this crystallised and was collected. The aqueous solution was proved to contain a nitrite. The substance was readily soluble in most organic solvents, but sufficiently sparingly so in methyl alcohol for purposes of crystallisation. It was obtained in pale yellow needles melting at 85°:

0·1262 gave 0·1936 CO_2 and 0·0462 H_2O. C=41·8; H=4·1.
$C_9H_{10}O_7N_2$ requires C=41·9; H=3·9 per cent.

The constitution of this compound follows from its conversion by heating during three days in a sealed tube at 100° with methyl-alcoholic ammonia into the dinitrodiaminoanisole described above, and confirmation is found in the observation that on reduction a diamine is produced which does not condense with phenanthraquinone to a derivative of phenazine.

UNIVERSITY OF LIVERPOOL. [*Received, July 18th,* 1918.]

LVI.—*The Propagation of Flame through Tubes of Small Diameter.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

IT has been shown in a previous communication (T., 1917, **111**, 1044) that the speed of the "uniform movement" of flame in a given mixture of methane and air is dependent on the diameter of the tube along which the flame travels, being enhanced by the action of convection currents in tubes of large diameter and reduced by conduction of heat by the walls in tubes of small diameter.

If the diameter of the tube is sufficiently small, the "uniform movement" of flame does not develop, but the flame dies out after travelling a few centimetres. Still further reduction in the diameter of the tube renders it impossible for the flame to spread

any measurable distance from the point of ignition. This fact was discovered by Davy, and was the starting point of his researches on the construction of a safe lamp for use in coal mines, his observation being: "I found that in tubes of 1/7-inch in diameter explosive mixtures"—of firedamp and air—"could not be fired when they were opened in the atmosphere" ("Collected Works," Vol. 6, p. 11).

Schloësing and de Mondésir (quoted by St. Claire Deville, "Leçon sur la Dissociation," p. 46) and Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 319) experimented on this subject, and the last-named have placed on record the speeds of flame in a mixture of methane and air containing 10·4 per cent. of methane, using tubes of glass of different diameters, as follow:

Diameter of tube, mm.	3·2	5·5	8·0	9·5	12·2
Speed of flame, cm. per sec....	nil	22	39	41	47

The methane used by Mallard and Le Chatelier was prepared from sodium acetate, and was impure; nevertheless, their observation that flame would not propagate in glass tubes of 3·2 mm. internal diameter is in fair agreement with Davy's statement (one-seventh of an inch is equal to 3·63 mm.).

Following on his discovery that a tube of small diameter would not allow flame to pass through it, Davy experimented with other means of exposing a cooling surface to the flame, such as perforated plates and systems of concentric tubes, and finally produced his wire gauze safety-lamp. A history of the development of the miners' flame lamp from Davy's original design would be out of place here, but it may be said that the retention of the wire gauze to protect the oil- or spirit-flame from inflammable mixtures of firedamp and air seems to have been regarded as essential by the majority of inventors. A few types of lamps have been constructed in which metal plates perforated with fine holes have been used, but no systematic experiments seem to have been recorded, on the lines of Davy's earlier experiments, to determine under what conditions tubes or perforated plates can be regarded as equivalent in safety to the gauze adopted, mainly for its convenience, by Davy.

In connexion with work on the construction of miners' safety-lamps, we have made a number of experiments on the speed of the uniform movement during the propagation of flame in mixtures of methane (firedamp) and air through tubes of small diameter;* on the passage of flame through similar tubes filled with mixtures

* It should be remembered that the uniform movement of flame is developed only when the inflammable mixture is contained in a tube closed at one end and open at the other, ignition being effected at or near the open end.

of methane and air and open at both ends; and on the passage or projection of flame through short tubes of small diameter.

The first series of experiments—on the uniform movement of flame—serves to demonstrate the increased cooling effect of the walls of the tube as its diameter is decreased, and may be regarded as an extension of the work already referred to (*loc. cit.*, p. 1050). The main results are shown in the table on p. 659; the numbers within brackets record distances, in cm., travelled by the flames before they became extinguished; the other numbers record the speeds of the flames in cm. per second, propagation taking place throughout the lengths of the tubes; the word nil indicates that flame could not be seen to spread an appreciable distance from the secondary discharge spark used to cause ignition. Ignition was, in each instance, at a point 3 cm. from the open end of the tube; the flame was allowed to travel 30 cm. from the point of ignition and its speed over a distance of 1 metre then measured; the tubes were 3 metres in length. Each recorded result is the mean of three or four closely agreeing determinations.

There are several points of interest in this table. The apparent limits of inflammability (horizontal propagation of flame) are narrowed as the diameter of the tube is decreased until with a tube 4·5 mm. in diameter only one of the mixtures tested (containing 9·95 per cent. of methane) would propagate flame.

No attempt was made to determine for each tube the exact limiting percentages of methane required for propagation of flame, but the table should supply fairly close approximations. Thus, the tube 5·6 mm. in diameter would have as its lower limit mixture one containing less than 8·5, but more than 8·25 per cent. of methane, and as its higher limit mixture one containing more than 10·5, but less than 10·65 per cent. Bearing in mind the fact that the exact limiting mixtures were not obtained, it will be seen that the speeds of the flames tend towards a constant value of about 35 cm. per sec. as the limiting mixtures are approached. This speed can be regarded as the slowest at which continued propagation of flame in mixtures of methane and air is possible.

It follows that the higher the coefficient of conductibility of the material of which tubes of small diameter are made, the narrower are the limits of inflammability for a tube of given diameter and the larger is the diameter of tube capable of preventing the spread of flame in any mixture. Thus Davy (*loc. cit.*) found that "metallic tubes prevented explosion better than glass tubes."

In Fig. 1 a curve is given showing the relationship between the speed of the uniform movement in a 9·95 per cent. methane–air mixture and the diameter of the tube (of glass) along which the

Internal diameter of tube. Mm.	Methane in mixture. Per cent.																
	7·6	8·0	8·25	8·4	8·5	9·0	9·5	9·95	10·15	10·5	10·65	10·8	11·0	11·5	11·6	11·65	12·0
3·6	nil	nil	nil	nil	nil	nil	nil	nil*	nil	nil	nil	nil	nil	nil	nil	nil	nil
4·5	nil	nil	(20)	(18)	(20)	(20)	(20)	33·5	nil	nil	nil	nil	nil	nil	nil	nil	nil
5·6	(25)	(20)	(27)	—	36·3	38·4	40·8	41·2	40·8	38·4	nil†	nil†	nil	nil	nil	nil	nil
7·2	(37)	(30)	(30)	(30)	38·0	40·5	46·8	46·3	44·5	42·9	(60)	(53)	(43)	nil†	nil†	nil†	nil
8·1	(45)	(30)	(35)	36·5	39·3	42·4	47·7	47·4	46·7	44·0	42·2	41·0	(45)	(50)	—	—	(60)
9·0	(55)	32·6	34·8	—	40·4	44·4	48·9	48·0	47·9	46·5	45·5	—	42·5	36·9	35·5	(60)	(60)

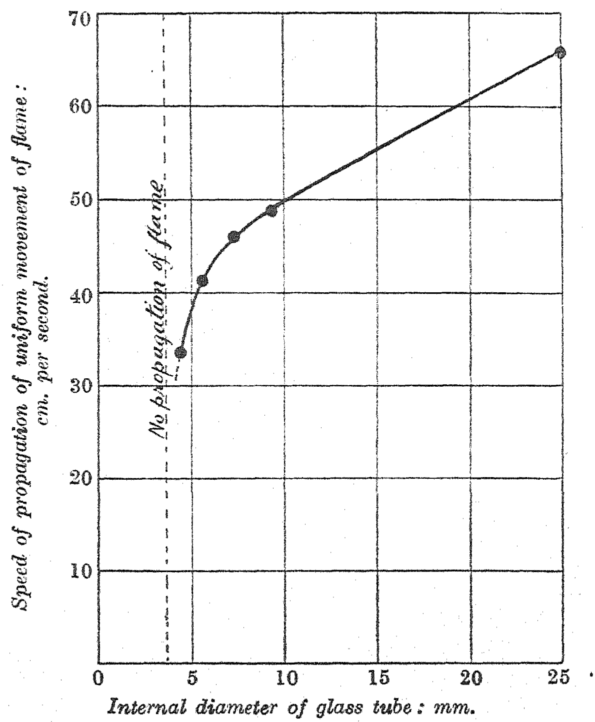
* When the flame was started in a tube 5·6 mm. in diameter and 8 cm. long it travelled 30 cm. along the 3·6 mm. tube and then died out.

† Flame travelled towards the open end of the tube, a distance of 3 cm.

flame travelled. This curve is a continuation of that shown in Fig. 4 in T., 1917, **111**, 1053, and should be compared therewith.

The Passage of Flame through Tubes Open at Both Ends.—When a mixture of methane and air contained in a horizontal tube open at both ends is ignited near one end of the tube, flame begins to travel with increasing speed towards the other end.* After a certain distance of travel, the flame vibrates backward and for-

FIG 1.



ward, and, in tubes of small diameter, becomes extinguished during any particularly rapid vibration. The distance travelled by the flame before vibrations begin depends on the length and diameter of the tube and on the percentage of methane in the mixture, being greater the longer is the tube and the larger its diameter, and less the nearer the percentage of methane approaches that required to give the fastest speed of flame (9·5 to 10 per cent. of methane in air).

* Unless the mixture is a "limit mixture," when the speed of the flame is uniform throughout its progress.

It thus results that a length of tube of diameter small enough to prevent the passage of flame in a mixture containing, say, 10 per cent. of methane in air, may fail to do so when the mixture contains only, say, 7 per cent., despite the fact that the flame in the former mixture has the greater speed. For the reason that with the 10 per cent. mixture vibrations, engendered by the rapidity with which the flame begins to move, may cause self-extinction of the flame, whilst with the 7 per cent. mixture the flame may move comparatively slowly and undisturbed throughout its course.

This fact is illustrated in the series of experiments recorded in the table that follows. The tubes were of glass and were 100 cm. long:

	Distances travelled by flame in tubes open at both ends.		
Percentage of methane in mixture	10·0	8·5	7·5
Internal diameter of tube.			
3·6 mm.	nil.	nil.	nil.
4·4 ,,	11·5 cm.	10 cm.	75 cm.
6·4 ,,	14	25 to 30	15 to 20
7·2 ,,	20 to 25	throughout	throughout.

Experiments of a similar nature were made with tubes of brass. The brass tubes were used as connexions between two open glass tubes 2·5 cm. in diameter and 10 cm. long, as described in the experimental portion of this paper, and their lengths were gradually shortened until flame passed from one glass tube to the other, when a mixture of methane and air was ignited near the open end of one of them. Two series of experiments were made; in one the propagation of flame was horizontal, in the other from below upwards. The results can be tabulated as shown on p. 661.

The lengths of brass tube recorded in this table represent relative distances of travel of the flames, the actual distances travelled being from 1 to 1·5 cm. less in each instance. The results for horizontal propagation of flame are shown graphically in Fig. 2, from which the greater precautions necessary to prevent the passage of flame in mixtures containing the lower percentages of methane is apparent.

The conditions under which an inflammation of firedamp takes place within a miners' safety-lamp depend on the construction of the lamp and on the manner in which it is manipulated. With some types of lamps (those receiving their air-supply from below the wick), the conditions are similar to those obtaining in the experiments just described. With others—and these constitute the majority of types—the air-supply reaches the wick from above, so that when firedamp is present in the air an inflammable mixture may occupy most of the upper portion of the lamp before it becomes

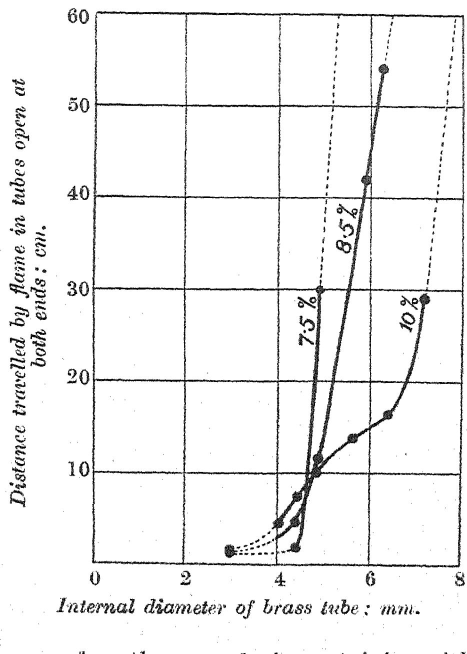
Lengths of brass tube required to prevent the passage of flame. Cm.

Percentage of methane in mixture.	10·0		8·5		7·5	
Internal diameter of tube. Mm.	Horizontal propagation.	Upward propagation.	Horizontal propagation.	Upward propagation.	Horizontal propagation.	Upward propagation.
3	less than 2	less than 2	less than 2	less than 2	less than 2	less than 2
4	4 to 5	5 to 6	2 to 3	5	less than 2	less than 2
4·4	7·5	9	4 to 5	7·5	less than 2	less than 2
4·8	10	11·5 to 12·5	11·5	18 to 19	30	30
5·6	14	15 to 16	42 to 43	50	—	—
6·4	16	18	54	55	—	—
7·2	29	32	more than 60	more than 60	—	—

ignited. Ignition is then as if near the closed end of a tube open at the other end.

Experiments were made in which a glass tube 12 cm. long and 2 cm. in diameter, closed at one end, was used as an explosion-vessel. Brass tubing of different diameters could be attached to the open end and determinations made of the lengths required to prevent the transmission of flame to an inflammable mixture of methane and air when a similar mixture was ignited by a secondary discharge 15 mm. from the closed end of the explosion-vessel, the apparatus being fixed horizontally.

FIG. 2.



With mixtures of methane and air containing either 10 or 7·5 per cent. of methane, the passage of flame from the explosion-vessel to the atmosphere outside was prevented by less than 2 cm. length of brass tubing of any diameter up to the largest tried, namely, 8 mm. In many instances, tongues of slightly luminous gases were projected from the ends of the brass tubes, but inflammation of the surrounding mixture did not follow. The question therefore arose whether increasing the speed of projection of these hot gases, by increasing the length of the explosion-vessel, would enable them to retain sufficient heat to ignite a mixture of methane

D D* 2

and air even after their passage through a considerable length of brass tubing of small diameter.

Experiments were therefore made in which explosion-vessels, 2 cm. in diameter, of different lengths were employed, so that the flames in 10 per cent. mixtures of methane and air, ignited at the closed ends of the explosion-vessels, would acquire different speeds by the time they reached the open ends. Previous experiments had shown that the speed of flame in a 10 per cent. mixture of methane and air contained in a horizontal glass tube 2 cm. in diameter, closed at one end and open at the other, increases progressively with its distance of travel from the closed end over distances of 3 or 4 metres. The results were as follow:

Length of explosion-vessel. Cm.	Length of brass tube required to prevent passage of flame in a 10 per cent. methane–air mixture. Cm.			
	12	20	30	40
Internal diameter of brass tube. Mm.				
4	less than 2	less than 2	less than 2	3 to 4
4·4	,,	3 to 4	,,	3 to 4
4·8	,,	13 to 14	16 to 18	more than 30
5·6	,,	16 to 18	24 to 25	,,
6·4	,,	18 to 19	more than 30	,,
7·2	,,	19 to 20	,,	,,
8·0	,,	19 to 20	,,	,,

The increased speed imparted to the heated products of combustion by increasing the speed of the flame thus materially reduces the protection against inflammation of the external atmosphere afforded by brass tubes. A miners' safety-lamp, however, rarely has an effective length of "explosion-vessel" exceeding 12 to 15 cm. On the other hand, its diameter is often as great as 6 cm. It seemed possible that the use of an explosion-vessel of larger diameter than that employed in the series of experiments just described might have an effect similar to increasing its length, inasmuch as the higher pressures produced within a vessel of greater capacity would project the heated products of combustion through the brass tubes with greater speed.

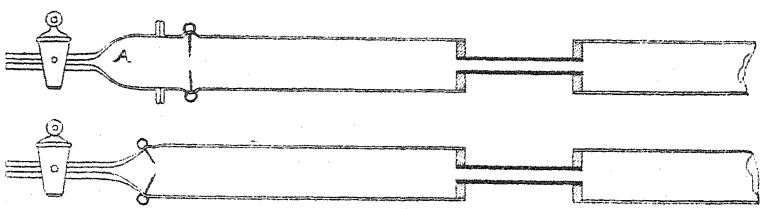
On trial, however, this was found not to be so. An explosion-vessel 7·5 cm. in diameter and 12 cm. long was no more effective in transmitting inflammation through brass tubes to the external atmosphere than one 2 cm. in diameter. Furthermore, when the length of this larger explosion-vessel was increased to 40 cm., it was found that protection was still afforded by a length of brass tube of less than 2 cm. of any diameter up to 8 mm., the largest tried. Increasing the capacity of the explosion-vessel thus actually

decreased the danger of the inflammation being conveyed to the external atmosphere.

These results, which were repeated many times with mixtures of different methane-content, are in conformity with some remarkable experiments by Beyling ("Verein für die Bergbaulichen Interessen im oberbergamtbezirk Dortmund." Essen, 1906), made primarily to determine the best means of rendering electrical machinery flame-proof. Beyling used an explosion-vessel 33·5 cm. in diameter and 42·5 cm. long (capacity, 42 litres), and found that when a mixture of firedamp and air containing 9 per cent. of methane was ignited at one end of the vessel, a hole more than 4 cm. in diameter could exist at the other end without danger of a similar mixture outside being ignited.

The explanation of these results is that the products of combustion, being under a fairly high pressure within the explosion-vessels of large capacity, were rapidly expanded as they issued

FIG. 3.



through the holes or tubes, and were thus cooled below the temperature at which they could ignite the mixture outside.

EXPERIMENTAL.

The experimental work can be divided into two portions, that dealing with the speed of flame in tubes of small diameter, and that relating to the passage of flame through short lengths of such tubes from vessels filled with inflammable mixtures.

The motion of the most rapid flame studied was sufficiently slow to follow by eye, so that for the measurements of speeds it sufficed to record the times at which the flames made their appearance at fixed points along the tubes. This was done by the use of a tapping-key in electrical connexion with a chronograph.

The different forms of apparatus used in the experiments on the passage of flame through short lengths of tubes are shown in Fig. 3. The upper diagram illustrates the means employed to study the passage of flame through tubes open at both ends. The ground-

glass cover, *A*, was removed just before igniting the mixture by sliding it downwards, so as to avoid disturbance of the mixture within the tube. The whole apparatus, including the glass extension beyond the length of brass tube undergoing test, was filled with the requisite mixture by displacement of air, six times the volume of the apparatus being taken for displacement.

The lower diagram shows the arrangement when testing the conditions necessary for the passage of flame from a closed vessel, and is self-explanatory.

The methane used throughout the experiments was from fire-damp obtained from a blower in South Wales; it contained 2 per cent. of nitrogen as its only impurity. The mixtures were stored over water in metal or glass gas-holders of suitable capacity, and were analysed before use.

These experiments have been carried out for the Mines Department of the Home Office. They complete part of a research on miners' safety-lamps which will form the subject of an official report.

[*Received, July 12th*, 1918.]

LVII.—*The Relative Activities of Methyl, Ethyl, and* n-*Propyl Iodides with Sodium* α- *and* β-*Naphthoxides.*

By HENRY EDWARD COX.

THE reactivity of the alkyl iodides with a variety of compounds has been measured by many investigators.

It has usually been found that methyl iodide is many times more active than ethyl iodide, and ethyl iodide is from one to five times as active as *n*-propyl iodide; several anomalies have been recorded, however, including one instance in which ethyl iodide is twice as reactive as methyl iodide. It seemed of interest to examine the relative activities of these substances with further bases, and as the naphthoxides are very similar in chemical behaviour, it was decided to examine whether there is any difference in their reactivities with the alkyl haloids; methyl, ethyl, and *n*-propyl iodides were chosen, as it has been found in all recorded work that the higher members of the series show a perfectly regular and gradual diminution in activity with increasing molecular

weight, whereas the first three members have shown considerable divergence.

The following table shows the results on record for these iodides calculated in terms of *n*-propyl iodide = 1:

	Methyl.	Ethyl.	*n*-Propyl.
Triethylamine in acetone[1]	590·7	5·24	1·00
Sodium ethoxide in ethyl alcohol[2]	36·13	2·85	1·00
Potassium ethoxide ,, ,, ,, [2]	35·53	2·78	1·00
Sodium methoxide ,, ,, ,, [2]	16·31	2·51	1·00
Potassium methoxide ,, ,, [2]	16·41	2·45	1·00
Dimethylaniline ,, ,, ,, [3]	48·00	3·2	1·00
Tri*iso*amylamine ,, ,, ,, [3]	327·0	4·2	1·00
Sodium ethyl acetoacetate ,, [4]	39·2	4·2	1·00
Silver nitrate ,, ,, ,, [5]	0·94	2·2	1·00
Sodium phenoxide ,, ,, ,, [6]	12·1	2·5	1·00

[1] Menschutkin, *Zeitsch. physikal. Chem.*, 1890, **5**, 589.
[2] Hecht, Conrad, and Bruckner, *ibid.*, 1889, **4**, 273, 649.
[3] Preston and Jones, T., 1912, **101**, 1930.
[4] Wislicenus, *Annalen*, 1882, **212**, 239.
[5] Burke and Donnan, T., 1904, **85**, 555.
[6] Segaller, T., 1913, **103**, 1154.

There are also many figures on record for methyl and ethyl iodides only. In the above table, there is a very marked increase in activity of methyl iodide with triethylamine and with tri*iso*-amylamine, which contrasts very strongly with the fact that ethyl iodide is twice as reactive as methyl iodide with silver nitrate.

It is well known that the naphthols are esterified more readily than the phenols, so that it might be anticipated that the velocity constants would be higher than with phenoxides and lower than with ethoxides. This expectation is borne out by the results obtained.

Sodium α-naphthoxide is slightly more reactive than the β-compound, and it was found that the difference is slightly accentuated as the molecular weight of the alkyl group increases; thus at concentration $N/5$, the ratio k_α/k_β is:

Methyl iodide.....................	1·12
Ethyl iodide	1·23
n-Propyl iodide	1·32

This greater activity of the α-compound with *n*-propyl iodide makes the relative activity of the iodides rather less with the α- than with the β-naphthoxide. At the same concentration, $N/5$, was found:

	α-Naphthoxide.	β-Naphthoxide.
Methyl iodide	7·41	8·82
Ethyl iodide	1·99	2·16
n-Propyl iodide	1·00	1·00

These results all refer to the reaction in ethyl alcohol at 40°. The reaction is bimolecular, as is to be expected from the equation.

There is, however, a possibility of a side-reaction taking place, such as the formation of olefines or ethers. This is suggested by the fact that the velocity constant decreases slightly as the reaction proceeds; this decrease has been observed by nearly all workers with alkyl iodides. It does not seem probable that it is due to loss of alkyl iodide, as it is observed even at low temperatures and when working in sealed tubes. It is also observed in the presence of an excess of alkyl iodide. The decrease is not due to neutral-salt action, as it is found that addition of sodium iodide has no appreciable effect on the velocity constant.

It was also observed that, particularly in the more concentrated solutions, the reaction mixture, which is practically colourless at the start, darkens as the reaction proceeds. This takes place even though the flask is not opened or exposed to the air. The colour is not due to the liberation of iodine.

The question also arises whether the equation,

$$C_2H_5{\cdot}ONa + C_{10}H_7{\cdot}OH \longrightarrow C_2H_5{\cdot}OH + C_{10}H_7{\cdot}ONa$$

is reversible or not. If alcoholysis takes place, sodium ethoxide will be formed; the velocity coefficients for sodium ethoxide and the alkyl iodides are several times larger than those of the naphthoxides with the corresponding iodides. The velocity constant would therefore show a markedly higher value at the commencement of an experiment, and would rapidly fall off as the ethoxide disappears, and the increasing concentration of free naphthol retards the further alcoholysis of the naphthoxide. A rapid decrease in the value of the constant would be found if there is much alcoholysis.

In the experiments here described, there is a gradual diminution in the value of the constant, but it is not large; indeed, in most experiments it is not larger than the decrease observed by Hecht and Conrad in their work on the ethoxides, where the case of alcoholysis does not arise. In order to obtain some information on this point, experiments were made in $N/10$-solution with methyl iodide and sodium α- and β-naphthoxides containing 5 per cent. excess of the corresponding naphthol; this would suppress alcoholysis, and consequently decrease the constant. The effect observed was that the constant is decreased by 7·3 per cent. in the case of the α-naphthoxide and by 10·7 per cent. in the case of the β-naphthoxide, but there was still observed the gradual decrease in the value of k.

The effect of the increased viscosity by the excess of naphthol

would no doubt slightly decrease the constant, but not to so great an extent. It is interesting to note that Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474) found that a decrease of 7 per cent. was produced by 5 per cent. excess of phenol in the reaction between sodium phenoxide and methyl iodide at concentration $N/2$.

Effect of Initial Concentration on the Velocity Coefficients.

This point is one of considerable importance. Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1890, **5**, 289) proposed the formula $k_v = k_1 + a \log v$, where v is the volume in litres which would contain one gram-molecular weight of the reacting substances.

This empirical equation has been found to hold remarkably well in several reactions of the kind here considered. Schröder and Acree (T., 1914, **105**, 2582) have given a scientific basis to this equation, which greatly enhances its interest. They show also that at a given dilution corresponding with complete ionisation of one of the reacting substances, the equation would no longer hold.

The effect of initial concentration has been tried by measuring the velocity of the reaction in equivalent concentrations from $N/1$ to $N/40$. The velocity coefficient increases with dilution in each case, and it increases more rapidly in the case of the α-naphthoxide than with the β-naphthoxide.

The increase is large with methyl iodide, less with ethyl and still less with n-propyl iodide; this is quite in accord with the results of Hecht, Conrad, and Brückner. The equation $k_v = k_1 + a \log v$ is found to hold for ethyl and propyl iodides at least up to dilution $v = 40$. With methyl iodide and the α- and β-naphthoxides, the equation holds from $v = 1$ up to $v = 10$ and $v = 7$ respectively; thereafter the value of k_v increases abnormally rapidly. Figs. 1 and 2, obtained by plotting actual values of k against $\log v$, show the increase with dilution. Each point lying off the straight line has been determined in duplicate.

It is most unlikely that ionisation of the naphthoxides would be complete at as low a dilution as $N/10$, so that Schröder and Acree's prediction cannot be applied.

Also, if the increase is due to alcoholysis or ionisation, or to any change in the naphthoxide, it would be expected that a similar rise would be observed with ethyl and propyl iodides at perhaps slightly greater dilution.

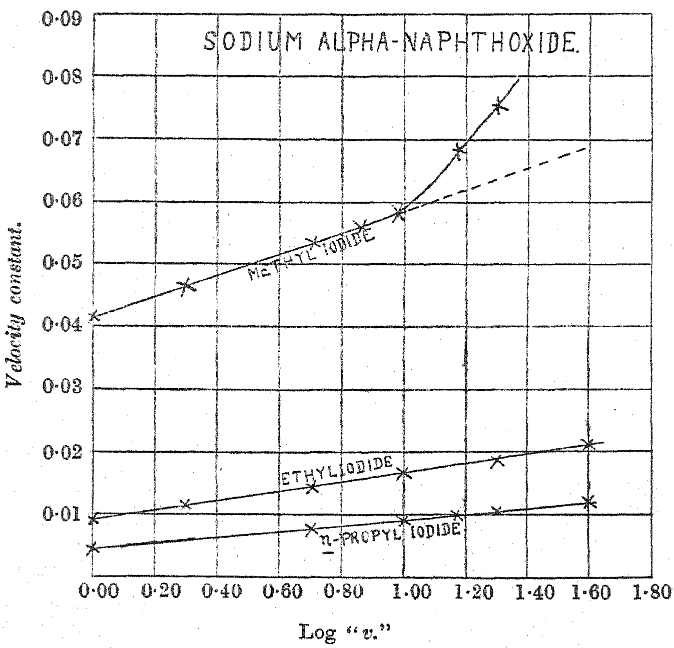
Up to $v = 40$, no such rise is observed, so that it appears probable that this abnormality is due to some specific effect with methyl iodide only.

EXPERIMENTAL.

All the reactions were carried out with ethyl alcohol as solvent; the alcohol was prepared by digesting commercial absolute alcohol with calcium oxide and calcium for several hours, and then redistilling from calcium.

The naphthoxides were prepared from the purest obtainable α- and β-naphthols, quite white, melting at 94° and 122° respectively. The calculated quantity of sodium dissolved in ethyl alcohol was added to an alcoholic solution of the naphthol, and the

FIG 1.



solution evaporated to dryness in a vacuum at 100°. The products were almost white. (Found: Na=13·75 and 13·87 respectively. Calc.: Na=13·86 per cent.)

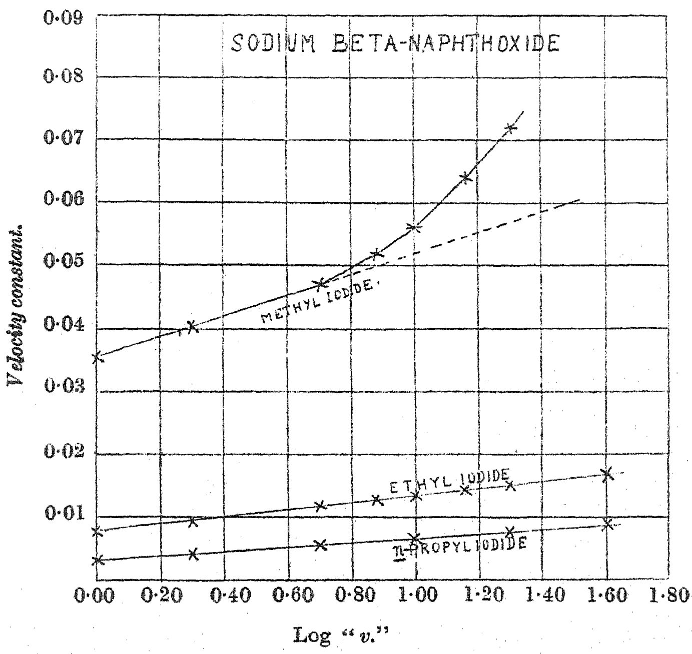
Some of the duplicate experiments were made by mixing solutions of sodium ethoxide and naphthol in the proper proportions just before use. This method gave results identical with those obtained by weighing out the dry compound, and has been applied

successfully by Hecht and Conrad and by Robertson and Acree in their work on phenoxides. It is very convenient in the case of the α-naphthoxide, as this salt is very sensitive to air and moisture and rapidly turns brown on exposure.

Tymstra and Eggink's method (*Ber.*, 1906, **39**, 14) was tried, but without success, minute balls of sodium being retained even after prolonged heating.

Methyl and ethyl iodides were purified by washing with dilute alkali, then with water, drying over fused calcium chloride, and

FIG. 2.



redistilling from ignited silver. The boiling points were 42·5—43° and 71·5—72° respectively. *n*-Propyl iodide was obtained from propyl alcohol by Bancel's method (*Bull. Soc. chim.*, 1883, [ii], **39**, 648) and purified as above. It boiled at 101—101·5°.

The temperature was maintained at 40·0° by means of a thermostat fitted with an Ostwald toluene regulator and an efficient stirring gear.

The requisite quantities of reagents were weighed out, dissolved separately, and the solutions mixed. After allowing time for the

mixture to attain the temperature of the bath, 5 c.c. were withdrawn by a pipette, kept at 40°, calibrated to deliver a volume equal to 5 c.c. at 15°.

This was run into cold water containing almost enough standard hydrochloric acid to neutralise the unchanged naphthoxide, and the titration completed as rapidly as possible, using lacmoid as indicator.

The results were calculated from the equation $k' = \frac{1}{t} \cdot \frac{x}{a \cdot (a-x)}$, in terms of c.c. of acid used for titration, then brought to k in terms of gram-molecules per litre by multiplying by five times the dilution "v" of the acid. Time in minutes was reckoned from the time of the first titration when the mixture had attained the proper temperature.

Only one experiment with each pair of substances is given in full, the other results being summarised for economy of space.

Methyl Iodide.

Sodium α-naphthoxide. $N/1$ each. Acid $N/5$.

t.	$a-x$.	k'.
0	23·35	—
7	18·25	0·001719
15	14·70	0·001680
22	12·65	0·001646
30	1[illegible]·00	0·001603
37	9·75	0·001614
44	8·85	0·001595

Mean $k' = 0·001643$.
$k = k' \times 25 = 0·04108$.

Sodium β-naphthoxide. $N/1$ each. Acid $N/5$.

t.	$a-x$.	k'.
0	21·70	—
14	15·05	0·001454
21	13·05	0·001455
30	11·15	0·001454
41	9·65	0·001404
50	8·65	0·001390
60	7·75	0·001382

Mean $k' = 0·001423$.
$k = k' \times 25 = 0·03558$.

Ethyl Iodide.

Sodium α-naphthoxide. $N/5$ each. Acid $= N/10$.

t.	$a-x$.	$k' \times 10^3$.
0	9·85	
60	8·43	0·2850
130	7·18	0·2905
234	5·95	0·2845
290	5·43	0·2850
350	5·00	0·2813
410	4·65	0·2769

Mean $k' = 0·0002839$.
$k = k' \times 50 = 0·01420$.

Sodium β-naphthoxide. $N/5$ each. Acid $= N/10$.

t.	$a-x$.	$k' \times 10^3$.
0	9·70	—
85	8·08	0·2376
160	7·10	0·2359
235	6·33	0·2335
300	5·78	0·2330
360	5·43	0·2251
420	5·05	0·2260

Mean $k' = 0·0002318$.
$k = k' \times 50 = 0·01159$.

n-*Propyl Iodide.*

Sodium α-naphthoxide. $N/10$ each. Acid $= N/20$.

t.	$a-x$.	$k' \times 10^4$.
0	9·55	—
140	8·55	0·8748
247	7·90	0·8856
384	7·30	0·8406
540	6·65	0·8456
586	6·48	0·8464
630	6·35	0·8376

Mean $k' = 0·00008551$.
$k = k' \times 100 = 0·008551$.

Sodium β-naphthoxide. $N/10$ each. Acid $= N/20$.

t.	$a-x$.	$k' \times 10^4$.
0	9·65	—
140	8·85	0·6693
247	8·35	0·6532
384	7·80	0·6402
540	7·25	0·6353
587	7·02	0·6616
630	6·90	0·6555

Mean $k' = 0·00006525$.
$k = k' \times 100 = 0·006525$.

Summary of Results.

Methyl Iodide.

Sodium α-naphthoxide.

v.	k_v (found).	k_v (calc.).
1	0·04108	0·04108
2	0·04693	0·04623
5	0·05307	0·05303
7·5	0·05555	0·05604
10	0·05864	0·05818
15	0·06844	—
20	0·07513	—

"a" $= 0·0171$.

Sodium β-naphthoxide.

k_v (found).	k_v (calc.).
0·03556	0·03556
0·04060	0·04059
0·04725	0·04723
0·05235	0·05019
0·05590	—
0·06487	—
0·07209	—

"a" $= 0·0167$.

Ethyl Iodide.

Sodium α-napthoxide.

v.	k_v (found).	k_v (calc.).
1	0·009185	0·009185
2	0·01166	0·01135
5	0·01422	0·01422
7	—	—
10	0·01636	0·01638
15	—	—
20	0·01860	0·01855
40	0·02109	0·02072

"a" $= 0·00720$.

Sodium β-naphthoxide.

k_v (found).	k_v (calc.).
0·007900	0·007900
0·009908	0·009646
0·01159	0·01195
0·01250	0·01280
0·01402	0·01370
0·01453	0·01472
0·01568	0·01545
0·01700	0·01719

"a" $= 0·00580$.

n-*Propyl Iodide.*

Sodium α-naphthoxide.

v.	k_v (found).	k_v (calc.).
1	0·004300	0·004300
5	0·007133	0·007355
10	0·008551	0·008670
20	0·01011	0·009985
40	0·01121	0·001130

"a" $= 0·00437$.

Sodium β-naphthoxide.

k_v (found).	k_v (calc.).
0·003160	0·003160
0·005355	0·005431
0·006525	0·006410
0·007392	0·007388
0·008517	0·008367

"a" $= 0·00325$.

Sodium α-naphthoxide containing 5·0 per cent. excess of α-naphthol with methyl iodide, $N/10$ each.

$k=0\cdot05436$; decrease in $k=7\cdot30$ per cent.

Sodium β-naphthoxide containing 5·0 per cent. excess of β-naphthol with methyl iodide, $N/10$ each.

$k=0\cdot04989$; decrease in $k=10\cdot75$ per cent.

Conclusions.

The reaction of the alkyl iodides with sodium α-naphthoxide and sodium β-naphthoxide is a bimolecular one of a special type, in which the velocity of reaction is dependent on the initial concentration.

There is some evidence that both naphthoxides undergo alcoholysis in ethyl-alcoholic solution.

Sodium α-naphthoxide is more reactive towards the alkyl iodides than is sodium β-naphthoxide.

The presence of an excess of α- or β-naphthol decreases the velocity coefficient.

The velocity of the reaction in each case increases with dilution. The increase is most marked with methyl iodide, and becomes less as the molecular weight of the alkyl group increases.

The velocity of reaction at dilution "v" can be expressed in the form of an equation $k_v=k_1+a\log v$. This equation holds good with ethyl and n-propyl iodides at least so far as dilution $v=40$. With methyl iodide, the equation holds only up to dilution $v=10$ for sodium α-naphthoxide and $v=7$ for the β-compound; at higher dilution, methyl iodide exhibits abnormal reactivity.

The order of relative activity is methyl, ethyl, n-propyl. Methyl iodide is several times more active than ethyl iodide at the same dilution; this is in agreement with the majority of the published results for these iodides.

The author wishes to express his thanks to Mr. G. R. Thompson, who has provided every facility for this work; also to Dr. J. C. Crocker for his kind interest and valuable advice.

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[*Received, June 22nd,* 1918.]

LVIII.—*The Ternary System—Sodium Sulphate, Ammonium Sulphate, and Water. The Utilisation of Nitre Cake for the Production of Ammonium Sulphate.*

By HARRY MEDFORTH DAWSON.

IN connexion with experiments instituted with the object of finding a method for the separation of sodium sulphate and ammonium sulphate from solutions containing both these substances, and with a view to the possible use of solutions of nitre cake for the absorption of ammonia in the manufacture of ammonium sulphate, an investigation has been made of the equilibrium relations in the system Na_2SO_4–$(NH_4)_2SO_4$–H_2O. This investigation was completed during 1917, and although it was originally intended to defer the publication of the results for the present, the appearance of a series of papers by Matignon and Meyer (*Compt. rend.*, 1917, **165**, 787; 1918, **166**, 115, 686) on the equilibrium conditions in this system has led the author to revise his original proposal.

The components of this system combine to form two compounds, namely, Glauber's salt and the double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$, and the characteristic features of the system are largely determined by the properties of these compounds. The double salt seems to have been first obtained by Séguin (*Ann. Chim. Phys.*, 1814, **91**, 219), and subsequently its formation by the interaction of ammonium chloride and Glauber's salt and by the action of water on a mixture of sodium chloride and ammonium sulphate was described by Schiff (*Annalen*, 1860, **114**, 68). The crystallographic properties of the double sulphate have been examined on several occasions by Mitscherlich (*Ann. Phys. Chem.*, 1843, [ii], **58**, 469), Lang (*Wien Akad. Ber.*, 1862, **45**, 108), Reinsch (*Zeitsch. Kryst. Min.*, 1884, **9**, 561), and Retgers (*Zeitsch. physikal. Chem.*, 1891, **8**, 58), but the conditions of formation of the double salt and its relation to the simple salts do not appear to have been previously examined. According to Retgers (*loc. cit.*), crystals of the anhydrous double sulphate separate out at temperatures between 50° and 70°, but the crystals actually obtained by this observer were very small and impure, and the view that they represent the anhydrous double sulphate was based on the optical behaviour of the crystals when examined under the microscope.

In preliminary experiments, it was found that finely powdered Glauber's salt and ammonium sulphate react together at the

ordinary temperature, the mixture becoming pasty and the temperature falling considerably. Although it was at first suspected that this might be due to the simple dehydration of the Glauber's salt in the presence of ammonium sulphate, further experiments showed that the reaction consists in the formation of the double salt in accordance with the equation

$$Na_2SO_4,10H_2O + (NH_4)_2SO_4 = Na_2SO_4,(NH_4)_2SO_4,4H_2O + 6H_2O.$$

If the finely powdered substances are mixed together whilst the temperature is kept at $-15°$ to $-20°$, there is no evidence of the above reaction, the mixture remaining perfectly dry, but at $-10°$, on the other hand, the mixture shows distinct signs of caking, and it thus seemed probable that the above reaction sets in at some temperature between $-10°$ and $-20°$.

Lowering of the Temperature of Transition of Glauber's Salt on the Addition of Ammonium Sulphate.—In experiments made to determine the effect of ammonium sulphate on the temperature at which Glauber's salt is transformed into anhydrous sodium sulphate, about 100 grams of Glauber's salt were heated to about 40° and cooling curves taken before and after the addition of measured quantities of ammonium sulphate. During the cooling, the tube containing the mixture was surrounded by cotton-wool and the mixture thoroughly stirred. The results obtained are shown in table I.

TABLE I.

Reference number.	Nature of cooling system.	Transition temperature.
a	Glauber's salt.	32·35°
b	100 grams Glauber's salt + 4·66 grams $(NH_4)_2SO_4$	30·05
c	,, ,, + 9·33 ,, ,,	27·75
d	,, ,, + 18·65 ,, ,,	26·50
e	,, ,, + 26·60 ,, ,,	26·50
f	,, ,, + 43·8 ,, ,,	continuous fall in temperature.

The value of the molecular lowering of the transition temperature calculated from observations *b* and *c* is 65, which is slightly less than the value obtained by Loewenherz (*Zeitsch. physikal. Chem.*, 1895, **18**, 70) for relatively dilute solutions of the alkali sulphates. The limiting temperature, 26·5°, obviously represents an invariant point, and, in point of fact, the three solid phases in equilibrium with the solution are Glauber's salt, anhydrous sodium sulphate, and the double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$.

Decomposition of the Double Salt.—In view of Retgers's observation that the crystals deposited at higher temperatures are anhydrous, it was to be expected that the double salt would decom-

pose at some temperature below 70°. Preliminary experiments, in which a dilatometer was filled with the finely powdered double salt, gave no positive evidence of this change. On the other hand, when a mixture of 50 grams of Glauber's salt and 30 grams of ammonium sulphate was heated to about 80° and allowed to cool in the air, the temperature remained stationary at 58—59°. In a further experiment, in which the tube containing the mixture was jacketed and allowed to cool with the outside tube immersed in a water-bath at 50°, the temperature of the mixture fell slowly to 58·2° and then rose to 59·3°, at which it remained constant for a very considerable time. This temperature was evidently to be regarded as that corresponding with a further invariant point, and it seemed probable that this was the temperature of decomposition of the hydrated double salt.

Solubility Measurements.—Further information was sought by solubility measurements, the chief object of which was to ascertain the composition of the solutions which are characteristic of the invariant and univariant systems. In the case of the invariant systems, the solutions in question are saturated with respect to three solid phases, and the temperature has a definite value. On the other hand, the temperature is variable in the case of the univariant systems which are characterised by the presence of two solid phases, but at a given temperature the concentration of both the sodium sulphate and the ammonium sulphate has a definite value.

In connexion with the solubility measurements, a quantity of the double salt was prepared by dissolving sodium sulphate and ammonium sulphate in the molecular proportion 1:2 to give a solution of the approximate molecular composition

$$1000H_2O:40Na_2SO_4:80(NH_4)_2SO_4.$$

The warm solution was allowed to cool to the ordinary temperature, and crystals of the double salt were deposited, which, after drying in contact with the air, gave on analysis $Na_2SO_4=40·7$ (theory, 41·0 per cent.) and $(NH_4)_2SO_4=38·3$ (theory, 38·15 per cent.).

Preliminary measurements of the quantities of sodium and ammonium sulphates in the solutions saturated at 0°, 25°, 50°, and 100° were made in order to ensure the presence of the requisite solid phases in the subsequent experiments. In making the final determinations, a solution having approximately the composition of the saturated solution was prepared, and when the temperature of this had been brought to the desired value, the requisite solid phases in finely powdered form were added in considerable quantity. The mixture was stirred for one to two hours, and a sample of the saturated solution, filtered through a cotton-wool plug, was removed

for analysis. The sodium sulphate was estimated by evaporation of a measured fraction to dryness in a platinum dish, and subsequently heating the residue to redness. It was found advisable to treat the residue with a little ammonia, and to repeat these operations before the sodium sulphate was finally weighed. For the estimation of the ammonium sulphate, a second fraction was added to an excess of standard sodium hydroxide, and, after boiling, the excess of alkali was titrated by means of standard acid.

The results obtained in the solubility experiments are shown in table II, in which are recorded the temperature, the nature of the solid phases in contact with the solution, and also the weight and molecular composition of the solution.

The relations exhibited by the solubility data recorded in the table on p. 679 are shown in Fig. 1, in which temperature is given by the abscissa, whilst the ordinate represents the number of molecules of sodium sulphate *or* ammonium sulphate per 1000 molecules of water. Two groups of curves are thus obtained, the lower one of which has reference to the sodium sulphate content of the saturated solutions and the higher one to the amount of ammonium sulphate. Corresponding points in the two groups are indicated by the same letters, the ammonium sulphate group being distinguished by a dash. The points D and D' thus represent the numbers of molecules of sodium sulphate and ammonium sulphate respectively per 1000 molecules of water in the solution which is characteristic of the invariant system at the temperature of decomposition of the double salt into the component simple sulphates. In exactly the same way, the curves which connect such corresponding points are corresponding curves. The curves which represent solutions saturated with respect to Glauber's salt and ammonium sulphate (AB and $A'B'$), with respect to double salt and ammonium sulphate (BD and $B'D'$), and with respect to anhydrous sodium sulphate and ammonium sulphate (DE and $D'E'$), do not exhibit any peculiarity which calls for special comment. The case is different, however, when we consider the curves which correspond with solutions saturated with respect to double salt and Glauber's salt, and those which represent solutions saturated with respect to double salt and anhydrous sodium sulphate. The curves BC and $B'C'$ show that in solutions saturated in regard to double salt and Glauber's salt, the sodium sulphate content increases rapidly with rise of temperature, whilst the ammonium sulphate concentration rapidly decreases. Between $-16°$, which, according to the curves in Fig. 1, appears to be the temperature of formation of the double salt, and 26·5°, at which Glauber's salt is transformed into the anhydrous sulphate, the

TABLE II.

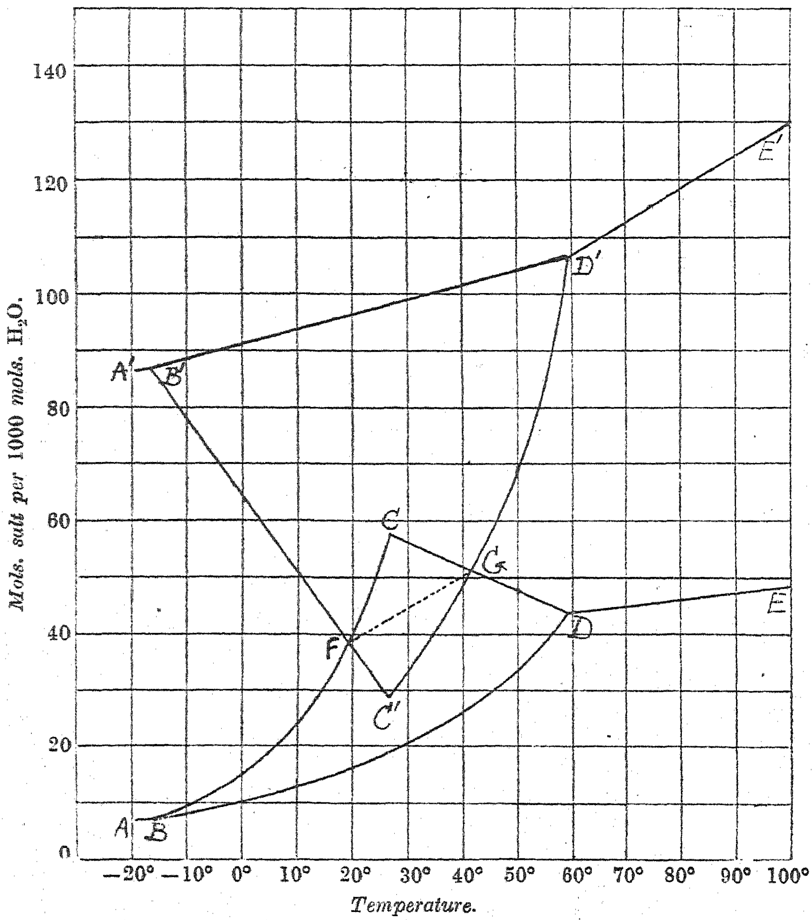
Temperature.	Nature of solid phases.	Grams per 100 of water: Na_2SO_4.	Grams per 100 of water: $(NH_4)_2SO_4$.	Mols. per 1000 of water: Na_2SO_4.	Mols. per 1000 of water: $(NH_4)_2SO_4$.
−19·5° (cryohydric temperature).	Ice, Glauber's salt, and ammonium sulphate	5·29	63·5	6·70	86·6
−18·0°	Glauber's salt and ammonium sulphate.	5·40	63·5	6·85	86·6
−16·0	Glauber's salt, ammonium sulphate, and double salt........	5·32	63·6	6·75	86·8
−13·0	Ammonium sulphate and double salt...	5·68	64·9	7·20	88·5
−10·0	,, ,, ...	6·33	65·6	8·03	89·2
0·0	,, ,, ...	7·81	66·7	9·9	91·0
15·0	,, ,, ...	10·85	69·6	13·75	94·9
25·0	,, ,, ...	14·6	71·0	18·5	96·8
40·0	,, ,, ...	19·7	75·1	25·0	102·4
50·0	,, ,, ...	25·8	76·1	32·7	103·8
−13·0	Glauber's salt and double salt	6·52	58·6	8·26	79·9
−10·0	,, ,, ...	7·78	56·1	9·86	76·5
0·0	,, ,, ...	12·05	46·6	15·25	63·5
15·0	,, ,, ...	22·9	33·3	29·0	45·4
20·0	,, ,, ...	31·5	28·9	39·9	39·4
25·0	,, ,, ...	40·9	22·1	51·8	30·2
26·5	Glauber's salt, double salt, and sodium sulphate	45·2	21·0	57·3	28·6
35·0	Sodium sulphate and double salt	41·7	28·7	52·9	39·2
40·0	,, ,, ...	40·5	34·7	51·3	47·3
50·0	,, ,, ...	37·2	50·5	47·2	68·9
55·0	,, ,, ...	36·0	62·0	45·6	84·6
25·0	Double salt	32·9	30·5	41·6	41·6
35·0	,, ...	37·3	34·7	47·3	47·3
59·3	Double salt, sodium sulphate, and ammonium sulphate........	34·3	77·7	43·5	106·0
75	Sodium sulphate and ammonium sulphate	36·1	84·3	45·7	115·0
100	,, ,,	37·9	95·0	48·0	129·5

molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution falls from about 12·8 to 0·50.

The curves *CD* and *C'D'*, which represent solutions saturated with respect to double salt and anhydrous sodium sulphate, follow an opposite course, in that the sodium sulphate content decreases

Fig. 1.

Na_2SO_4—$(NH_4)_2SO_4$—H_2O.



with rise of temperature, whilst the ammonium sulphate concentration increases rapidly. Between 26·5° and 59·3°, at which the double salt is decomposed, the molecular ratio of ammonium sulphate to sodium sulphate increases from 0·50 to 2·44.

The point *F*, at which the curves *BC* and *B'C'* intersect, and

the point G, corresponding with the intersection of CD and $C'D'$, represent respectively the lower and upper limits of the temperature interval within which the double salt is not decomposed in contact with water. The limiting temperatures are approximately 20° and 41·5° respectively, and it is only within this range that solutions saturated with respect to double salt and sodium sulphate (Glauber's salt below 26·5° and anhydrous sodium sulphate above 26·5°) contain a larger molecular quantity of sodium sulphate than of ammonium sulphate. Below 20°, the double salt is decomposed by water with the separation of Glauber's salt, and above 41·5° it is similarly decomposed with the separation of anhydrous sodium sulphate. The dotted curve joining the points F and G represents the curve of solubility of the double salt. In practice, it is possible to measure the solubility of the double salt at temperatures outside the interval corresponding with FG, but the saturated solutions so obtained are meta-stable.

The graph of the solubility data in Fig. 1 shows clearly that the two ammonium sulphate curves, as well as the two sodium sulphate curves, intersect at about −16°, and it is probable that this represents the temperature at which the double salt is formed from Glauber's salt and ammonium sulphate. Further evidence in support of the existence of this lower limiting temperature is afforded by observations on the cooling of certain mixtures of the components. Suitable mixtures are obtained by mixing finely powdered Glauber's salt and ammonium sulphate in the molecular proportion 2 : 3, with the addition of a little water to reduce the stiffness of the pasty mass which is formed by their interaction. The tube containing this mixture was fitted with a thermometer and stirrer, and surrounded by a wider glass tube immersed in a freezing mixture at −22°. The following readings were taken after successive five-minute intervals: −11·0°, −13·1°, −14·5°, −15·5°, −16·5°, −17·0°, −17·5°, −18·0°, −18·2°, −18·5°, −18·3°, −18·0°, −17·9°, −17·2°, −16·9°, −16·6°, −16·3°, −16·0°, −16·1°, −16·3°, −16·5°. According to this record, the temperature fell to −18·5° and then rose to −16·0°, which represents the temperature of formation of the double salt, and agrees closely with the temperature indicated by the solubility curves.

Crystallisation of Solutions containing Sodium and Ammonium Sulphates.—According to the graph of the solubility data in Fig. 1, it is evident that the crystallisation of a solution, which contains equimolecular quantities of the two sulphates, will yield the pure double salt if the temperature of the solution lies between 20° and 41·5°.

In an actual experiment, in which a solution, prepared by dis-

solving 284 grams of sodium sulphate and 264 grams of ammonium sulphate in 720 grams of water, was allowed to cool to 20°, 180 grams of the double salt were obtained. This result corresponds closely with that calculated from the equation:

$$1000H_2O : 50Na_2SO_4 : 50(NH_4)_2SO_4 = \\ 13{\cdot}0Na_2SO_4,(NH_4)_2SO_4,4H_2O + \\ 0{\cdot}948[1000H_2O : 39Na_2SO_4 : 39(NH_4)_2SO_4].$$

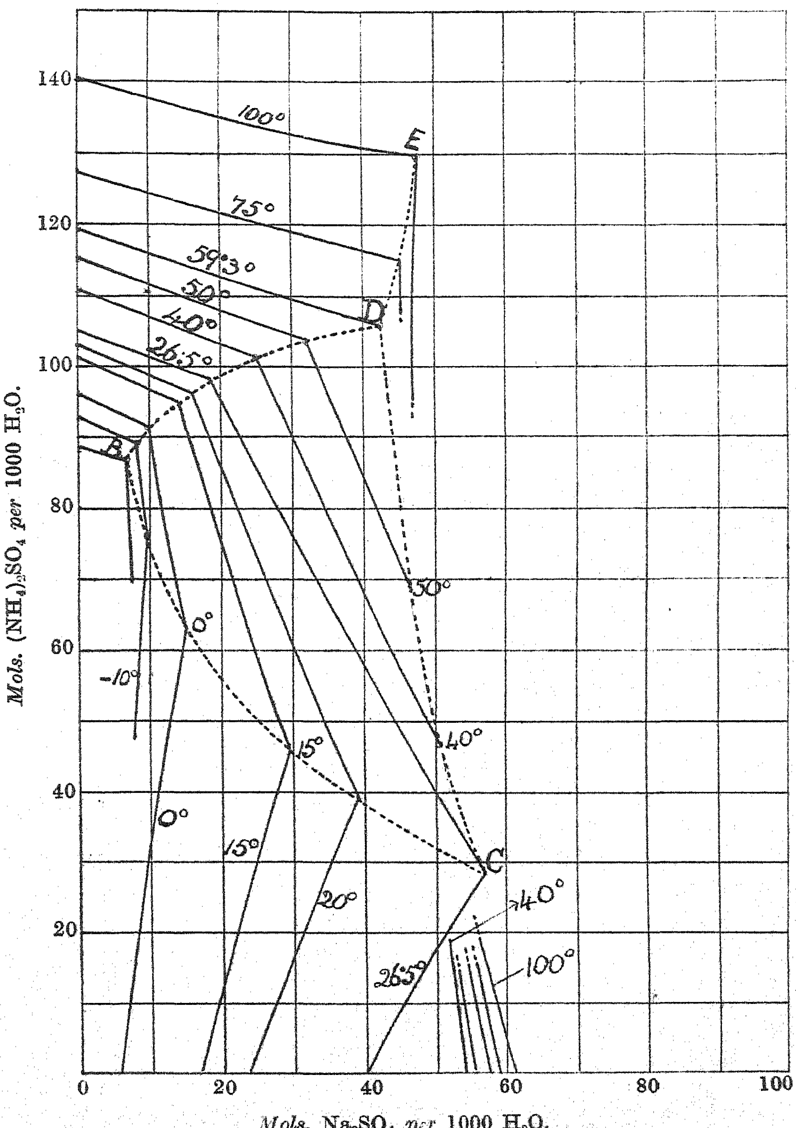
With regard to the separation of sodium and ammonium sulphates by crystallisation from a solution containing the mixed sulphates, it should be noted that there is a great disparity at low temperatures in the quantities of the two sulphates which are contained in solutions saturated with respect to Glauber's salt and ammonium sulphate or the double salt. For such solutions, the value of the molecular ratio of ammonium sulphate to sodium sulphate increases rapidly with rise of temperature until the ratio becomes equal to unity at the upper limit of the lower transition interval (20°). In view of the high value of the ratio at low temperatures, it is obviously possible to crystallise out a large proportion of the sodium sulphate from a solution containing sodium and ammonium sulphates by lowering the temperature.

Although Fig. 1 is well adapted to show the relationship between the double salt and the simple salts, the changes which occur on crystallisation may be more suitably discussed in reference to the curves which are shown in Fig. 2. In this diagram, the composition of any solution is represented by a single point. The horizontal axis gives the number of molecules of sodium sulphate per 1000 molecules of water, and the vertical axis the number of molecules of ammonium sulphate per 1000 of water. In the construction of this diagram, the required data for the solubility of sodium sulphate and of ammonium sulphate in water have been taken from the tables given in Landolt-Börnstein-Meyerhoffer. The isothermal curves connecting the points on the sodium sulphate and ammonium sulphate axes pass through the points which correspond with the saturated solutions recorded in table II. Below −16° and above 59·3°, the isothermals consist of two branches, and between these temperatures there are three branches on each isothermal. The isothermals actually represented on the diagram are those for −10°, 0°, 15°, 20°, 26·5°, 40°, 50°, 59·3°, 75°, and 100°. The sodium sulphate curves corresponding with the five highest temperatures are only indicated in so far as they do not interfere with the clearness of the diagram. The points *B*, *C*, and *D* correspond with the three invariant systems at −16°, 26·5°, and 59·3°, and are indicated by the same letters in Fig. 1.

The dotted curve *BD* represents the solutions which are saturated with respect to ammonium sulphate and double salt, *BC* those

FIG. 2.

Na_2SO_4—$(NH_4)_2SO_4$—H_2O.



which are saturated with respect to Glauber's salt and double salt, and *CD* those saturated with respect to anhydrous sodium sulphate and double salt. The region enclosed by the three curves corresponds with solutions which are saturated only with respect to the double salt.

By reference to Fig. 2, it is possible to predict what will occur when any solution containing sodium and ammonium sulphates is crystallised either by the removal of water at constant temperature or by a lowering of the temperature of the solution.

The diagram shows that the isothermal for 26·5° represents the maximum extension of the double salt curve, the molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution varying from 5·2 when saturation with respect to ammonium sulphate is reached to 0·50 when the solution becomes saturated with respect to sodium sulphate. From this it is apparent that, at this temperature, the double salt may be crystallised out from solutions of widely varying composition. On proceeding from 26·5° to higher or lower temperatures, the double salt isothermals undergo a gradual contraction until they disappear at $-16°$ and 59·3° respectively.

From the position of the dotted boundary curves on the diagram, it is evident that the solutions from which the double salt crystallises out between these limiting temperatures contain, in general, an excess of ammonium sulphate. At low temperatures, the required excess of ammonium sulphate is considerable, and for the most part solutions of the two sulphates when crystallised at low temperatures yield Glauber's salt as the solid product. If the concentration of the solution of the mixed sulphates is appropriately adjusted, a large proportion of the sodium sulphate may be removed in the form of Glauber's salt by cooling. Since the separation of Glauber's salt from the solution involves the removal of ten molecules of water for each molecule of sodium sulphate, it follows that the crystallisation will be accompanied by an automatic increase in the concentration of the ammonium sulphate.

The solubility data which determine the extent to which the separation of sodium and ammonium sulphates may be effected by crystallisation of Glauber's salt are recorded in table III for temperatures of $-10·0°$ and $-15·0°$. The successive columns give the temperature, the nature of the solid phases, the molecular composition of the solution in terms of 1000 molecules of water, and the molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution. The data cover the entire range of the Glauber's salt curves at the two temperatures, and by plotting the results it is possible to obtain the ratio of ammonium sulphate to

sodium sulphate in any solution which is saturated with respect to Glauber's salt at these temperatures.

TABLE III.

Temperature.	Nature of solid phases.	Molecules salt per 1000 mols. H_2O. Na_2SO_4.	$(NH_4)_2SO_4$.	Mol. ratio $\frac{(NH_4)_2SO_4}{Na_2SO_4}$.
$-10.0°$	Ice and Glauber's salt	7·32	47·2	6·45
-10.0	Glauber's salt	7·95	52·0	6·54
-10.0	,, ,, ...	8·51	60·4	7·10
-10.0	Glauber's salt and double salt	9·86	76·5	7·76
-15.0	Ice and Glauber's salt	7·48	69·7	9·3
-15.0	Glauber's salt	7·53	76·0	10·1
-15.0	Glauber's salt and double salt	7·20	84·0	11·7

The numbers in the last column show that the molecular ratio of ammonium sulphate to sodium sulphate in the solutions saturated with respect to Glauber's salt increases with increase in the ammonium sulphate content. Taking the value of the molecular ratio which corresponds with the middle portion of the isothermal, it follows that crystallisation at $-10.0°$ will yield a mother liquor containing about seven molecules of ammonium sulphate per molecule of sodium sulphate, and at $-15°$ a mother liquor containing ten to eleven molecules of ammonium sulphate per molecule of sodium sulphate.

If such mother liquors are evaporated at or about 100°, a large proportion of the ammonium sulphate present may be obtained in a pure condition. By reference to table II, it will be found that the solution saturated with respect to sodium sulphate and ammonium sulphate at 100° has the molecular composition

$$1000H_2O : 48{\cdot}0Na_2SO_4 : 129{\cdot}5(NH_4)_2SO_4.$$

For this solution, the molecular ratio of ammonium to sodium sulphate is equal to 2·7. If, therefore, we have a mother liquor for which, as a result of the separation of Glauber's salt by cooling to $-15°$, the molecular ratio of ammonium to sodium sulphate has been increased to 10·5 (compare table III), it follows that $\frac{10{\cdot}5-2{\cdot}7}{10{\cdot}5} \times 100 =$ approximately 75 per cent. of the contained ammonium sulphate may be obtained in pure condition by evaporation at 100°.

The relations exhibited by the equilibrium conditions at low temperatures and in the neighbourhood of 100° have been made the basis of a method for the production of ammonium sulphate and Glauber's salt by the treatment of solutions of the mixed sulphates such as are obtained when nitre cake or mixtures of

nitre cake and sulphuric acid are employed for the absorption of ammonia (Brit. Patent 114236, 1918). In this process, the liquor from the ammonia saturator has its concentration suitably adjusted, and is then cooled to about $-10°$, at which temperature a considerable proportion of the sodium sulphate separates out in the form of Glauber's salt. The mother liquor is then transferred to an evaporator, and on evaporation of the solution, crystals of ammonium sulphate are deposited until the molecular ratio of ammonium sulphate to sodium sulphate in the hot liquid has been reduced to a value not less than about 2·7. The residual liquor is then suitably diluted and returned to the refrigerator in admixture with a further quantity of solution from the saturator.

In view of the fact that the liquid from the saturator inevitably contains a certain amount of free acid, it was of some interest to investigate the influence of the presence of free sulphuric acid on the crystallisation of Glauber's salt at low temperatures. In these experiments, solutions containing fixed quantities of sodium sulphate and ammonium sulphate and variable quantities of free sulphuric acid were cooled to $-10·0°$, and the composition of the mother liquors was determined. The results obtained are recorded in table IV, in which the composition by weight and the molecular composition of the resulting solutions are shown, in addition to the value of the molecular ratio of ammonium sulphate to sodium sulphate.

TABLE IV.

	Grams per 100 of water.			Molecules per 1000 of water.			Mol. ratio
	Na_2SO_4.	$(NH_4)_2SO_4$.	H_2SO_4.	Na_2SO_4.	$(NH_4)_2SO_4$.	H_2SO_4.	$\frac{(NH_4)_2SO_4}{Na_2SO_4}$.
a	6·19	38·05	—	7·85	51·9	—	6·61
b	6·48	37·9	3·98	8·21	51·7	7·31	6·30
c	6·61	37·7	7·95	8·38	51·4	14·6	6·13

Although the ratio of ammonium sulphate to water in the three mother liquors is not quite the same, the values are sufficiently close to permit of a comparison of the effect of the free acid on the separation of the Glauber's salt, and it is evident from the table that the molecular ratio of ammonium sulphate to sodium sulphate in the solution decreases as the proportion of free acid increases. In other words, the separation of Glauber's salt is less complete in the presence of free acid, but the influence of the acid is not such as to affect seriously the efficiency of the cooling process. It may be noted that the mother liquor in experiment *c* contains about 5·2 per cent. of free sulphuric acid.

With regard to the influence of free acid on the separation of

ammonium sulphate by evaporation of the mother liquor obtained in the previous cooling process, it has been found that the molecular ratio of ammonium sulphate to sodium sulphate, which is characteristic of the acid-free solution when saturated with respect to sodium and ammonium sulphates at 100°, is not appreciably altered in the presence of a considerable quantity of free acid.

An experiment in which this ratio was determined in the presence of free sulphuric acid may be quoted. Fifty grams of a sulphuric acid solution of the approximate molecular composition, $1000H_2O:100H_2SO_4$, were placed in a tube provided with a stirrer and heated at 100°. Excess of finely powdered sodium and ammonium sulphates was added, and the mixture stirred for about an hour, when a sample of the solution was found to have the molecular composition,

$$1000H_2O:79{\cdot}6Na_2SO_4:224{\cdot}7(NH_4)_2SO_4:105{\cdot}4H_2SO_4.$$

The molecular ratio of ammonium to sodium sulphate in the saturated solution, which, it may be noted, contains about 15 per cent. of free acid, is thus 2·8, whilst the value of this ratio for the acid-free solution is 2·7.

The results of the observations in acid solutions lead to the conclusion that the presence of free acid in moderate quantities does not affect to more than a small extent either the separation of Glauber's salt by crystallisation at low temperatures or the separation of ammonium sulphate by evaporation of the resulting mother liquor.

Summary.

The equilibrium relations in the ternary system Na_2SO_4–$(NH_4)_2SO_4$–H_2O between −20° and 100° are described and illustrated by diagrams.

The characteristic features of the system are in a large measure determined by the double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$, which is formed from Glauber's salt and ammonium sulphate at −16°, and decomposes with the formation of the anhydrous simple salts at 59·3°.

Between −16° and 20°, the double salt is decomposed by water with the formation of Glauber's salt, and between 41·5° and 59·3° it is decomposed with the formation of anhydrous sodium sulphate.

The temperature at which Glauber's salt is transformed into the anhydrous sulphate is depressed to 26·5° by the addition of ammonium sulphate. At this temperature, the solution formed is in equilibrium with Glauber's salt, anhydrous sodium sulphate, and the double salt.

It is shown that sodium sulphate and ammonium sulphate may

be separated from one another by subjecting solutions of appropriate concentration to low temperatures, when most of the sodium sulphate crystallises out in the form of Glauber's salt. A large proportion of the ammonium sulphate in the mother liquor may be obtained in pure condition by evaporation at 100°.

The method of separation is not appreciably affected by the presence of moderate quantities of free sulphuric acid.

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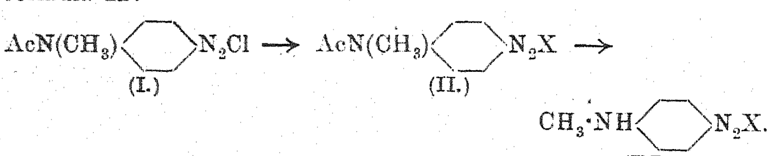
[*Received, July 27th*, 1918.]

LIX.—*Acylated* p-*Phenylenemethyldiamines*.

By GILBERT T. MORGAN and WILLIAM ROBINSON GRIST.

THE acyl derivatives of *p*-phenylenediamine have long had considerable technical importance, owing to the circumstance that these derivatives afford a practicable method of diazotising this diamine in both its amino-groups, a process required in the manufacture of bisazo-colouring matters containing the complex:

It has also been found that the monodiazonium salts (I) of the acyl derivatives of *p*-phenylenemethyldiamine are utilisable in the production of aminoazo-dyes (III), the acyl group being removed by hydrolysis from the intermediate product, which has the general formula II:



(I.) (II.) (III.)

In certain cases, the acylaminoazo-compounds themselves are found to have useful tinctorial properties (Morgan and Micklethwait, *J. Soc. Dyers*, 1909, **25**, 107; Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 296964).

The *p*-aminomethylacylanilides can be prepared by the following methods:

(i) From methylaniline, by successively acylating this base, nitrating its acyl derivative, and reducing the *p*-nitro-compound.

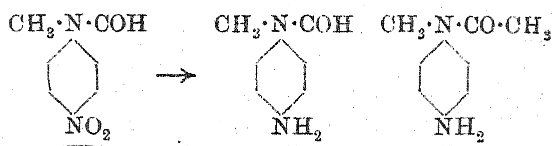
(ii) By methylating the acylanilide and then subjecting the methylacylanilide to the same treatment as in method (i).

(iii) Successive methylation and acylation of *p*-nitroaniline, followed by reduction of the resulting *p*-nitromethylacylanilide.

(iv) Methylation of the alkali derivative of 4:4′-dinitrodiazoaminobenzene, and hydrolysis of the methylated diazoamine to a mixture of chlorobenzene and methyl-*p*-nitroaniline, the secondary nitro-base being then acylated and reduced (Morgan and Alcock, T., 1909, **95**, 1332).

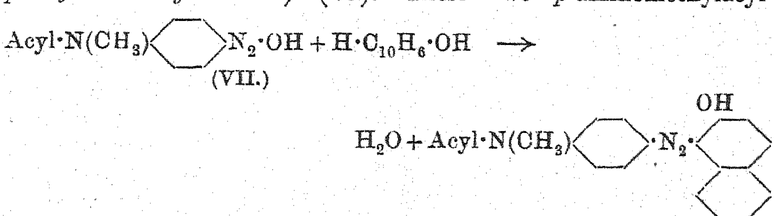
Of these four methods, the first is generally the most practicable providing that methylaniline is available in sufficient amount. Being in possession of considerable quantities of this base obtained by the process indicated in English Patent 514 of 1916, the authors have utilised this means of preparing several intermediate compounds from methylaniline which have not hitherto been described (Eng. Pat. 16520 of 1916).

p-*Nitromethylformanilide* (IV) is obtainable by nitrating methylformanilide, this acyl derivative being readily prepared by warming methylaniline with concentrated formic acid. It was shown that in the main product of this nitration the nitro-group enters the para-position with respect to the acylamino-complex, this orientation being demonstrated by hydrolysing the nitro-compound to *p*-nitromethylaniline and by converting this secondary base into its characteristic nitrosoamine.



(IV.) (V.) (VI.)

p-*Aminomethylformanilide* (as-*formyl*-p-*phenylenemethyldiamine*) (V) results from the reduction of the new nitro-derivative. Methylacetanilide, readily obtainable by mixing together methylaniline and acetic anhydride, is successively converted into *p*-nitromethylacetanilide and p-*aminomethylacetanilide* (as-*acetyl*-p-*phenylenemethyldiamine*) (VI). These two *p*-aminomethylacyl-



(VII.)

(VIII.)

anilides when treated with nitrous anhydride in dry acetone solution give rise to diazohydroxides (VII), which combine readily with dry β-naphthol, the condensation being accompanied by the elimination of a molecular proportion of water.

The *acylmethylaminobenzeneazo-β-naphthols* (VIII) thus produced are identical with the products obtained by successively diazotising the *p*-aminomethylacylanilides in aqueous solution and combining the diazonium salt with alkaline β-naphthol.

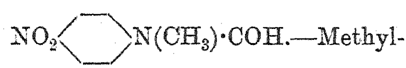
The foregoing diazohydroxides are obtainable as colourless, amorphous solids soluble in acetone and insoluble in ether or water.

p-Aminomethylbenzanilide and *p*-aminoethylbenzanilide when subjected to the action of nitrous anhydride in acetone solution yield only oily diazo-derivatives (compare Morgan and Alcock, *loc. cit.*).

EXPERIMENTAL.

I. p-*Aminomethylformanilide and its Acetyl Homologue.*

The starting point in these preparations was methylaniline, prepared by treating aniline with formaldehyde in the presence of zinc dust and sodium hydroxide (Eng. Pat. 514 of 1916). Methylformanilide was produced by heating the secondary base with one part of concentrated commercial formic acid for eight hours, and obtained as a viscid oil, which was extracted with benzene.

p-*Nitromethylformanilide*, —Methylformanilide (three parts) was dissolved in eight parts of cold concentrated sulphuric acid and nitrated with a mixture of two parts of nitric acid (D 1·42) and an equal volume of concentrated sulphuric acid. The nitration was carried out at 0° to 10°, and the product poured on ice. The pale yellow precipitate was crystallised from alcohol, when it separated in pale yellow, prismatic crystals melting at 118—120°:

0·1643 gave 23·2 c.c. N_2 at 20° and 752 mm. N = 16·03.

$C_8H_8O_3N_2$ requires N = 15·55 per cent.

When hydrolysed with hot concentrated hydrochloric acid, *p*-nitromethylformanilide yielded successively *p*-nitromethylaniline (m. p. 152°) and *p*-nitrophenylmethylnitrosoamine (m. p. 100°), thus demonstrating the orientation of the entrant nitro-group. The yield of *p*-nitromethylformanilide from a series of batches was about 70 per cent. The acid mother liquors slowly deposited a more readily soluble nitro-compound, which, being contaminated with resinous by-products, was not further investigated.

p-*Aminomethylformanilide* (as-*Formyl*-p-*phenylenemethyldiamine*).—*p*-Nitromethylformanilide (10 grams) was added gradually to a mixture of 10 grams of iron filings, 0·5 gram of formic acid, and 30 c.c. of water at 50°. The mixture was agitated vigorously, and the temperature, which tended to rise rapidly after each addition, was not allowed to exceed 75°. After the addition of all the nitro-compound, the heating was continued at this temperature for a few minutes, and the mixture was then treated with an excess of calcium carbonate and filtered quickly while hot. The *p*-aminomethylformanilide separated in feathery needles on cooling, and a further crop was obtained from the washings of the residue concentrated in a stream of carbon dioxide. The crude product was crystallised from water, separating therefrom in grey needles melting at 129—130°:

0·2213 gave 35·4 c.c. N_2 at 19° and 761 mm.* N=18·68.
$C_8H_{10}ON_2$ requires N=18·66 per cent.

p-Aminomethylformanilide was obtained by crystallisation from light petroleum in colourless needles melting at 132°. It darkened on exposure to light and air, especially when in a moist condition.

p-*Aminomethylacetanilide*.—Methylacetanilide was prepared by adding acetic anhydride (30 grams) to an equal weight of methylaniline. Much heat was generated, and, after cooling, the solution was poured into an equal volume of water. The acetyl compound remained oily for several days, but was caused to solidify by mixing with 2 c.c. of concentrated ammonia solution.

Methylacetanilide (m. p. 100°), recrystallised from alcohol, was dissolved in four parts of concentrated sulphuric acid and nitrated at 0° to 12° with 1·3 parts of nitric acid (D 1·42) mixed with an equal volume of concentrated sulphuric acid. The product obtained by pouring the solution on ice and crystallisation from alcohol melted at 153°. It was reduced by the method already described in the case of the formyl derivative (above).

p-Aminomethylacetanilide separated in brown needles, and was purified by crystallisation from hot water, when it was obtained in greyish-white needles melting at 60°:

0·1320 gave 18·4 c.c. N_2 at 19° and 768 mm. N=16·39.
$C_9H_{12}ON_2$ requires N=17·07 per cent.

Further crystallisation from light petroleum gave colourless needles of the base melting at 63°. On exposure to air, the base assumed a yellow colour.

* In this and subsequent analyses the nitrogen was measured over potassium hydroxide (50 grams in 100 grams of water).

II. *Diazo-derivatives of* p-*Aminomethylacylanilides.*

Formylmethylaminobenzene-4-diazohydroxide.—A solution of *p*-aminomethylformanilide in dry acetone (twenty-five parts) was cooled to $-10°$ and treated with excess of nitrous anhydride dissolved in the same solvent. The diazo-compound, which was obtained as a greyish-white, granular precipitate by the addition of cooled dry ether, darkened rapidly on exposure:

0·2060 gave 41·8 c.c. N_2 at 22·5° and 767 mm. N=23·55.
$C_8H_9O_2N_3$ requires N=23·46 per cent.

This product after drying over quicklime in a partial vacuum decomposed violently at 131—132°. When mixed with dry β-naphthol, the desiccated diazohydroxide combined to form an azo-derivative with loss of water, the mixture becoming damp.

Acetylmethylaminobenzene-4-diazohydroxide.—The foregoing treatment with nitrous anhydride applied to *p*-aminomethylacetanilide led to the production of a colourless, granular deposit of diazohydroxide precipitated by ether from the acetone solution. The product on exposure to air and light assumed a pale yellow colour:

0·2018 gave 38·8 c.c. N_2 at 22° and 766 mm. N=22·30.
$C_9H_{11}O_2N_3$ requires N=21·76 per cent.

The dried diazohydroxide decomposed violently at 131—132°, and when triturated with β-naphthol it combined to form an azo-derivative, water being eliminated.

Comparative experiments on the diazotisation of *p*-aminomethylbenzanilide and *p*-aminoethylbenzanilide with nitrous anhydride in acetone led only to oily diazo-derivatives which formed azo-compounds with β-naphthol and similar phenolic substances (compare Morgan and Alcock, T., 1909, **95**, 1323).

III. *Azo-derivatives of* p-*Aminomethylformanilide and* p-*Aminomethylacetanilide.*

Formylmethylaminobenzene-4-azo-β-naphthol,
$$COH{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$
—This compound was prepared by direct combination between formylmethylaminobenzene-4-diazohydroxide and dry β-naphthol or from the diazonium chloride of *p*-aminomethylformanilide prepared in aqueous solution and combined with alkaline β-naphthol. The azo-β-naphthol separated as a dark purple solid, insoluble in

aqueous alkalis, but dissolving in alcohol to a magenta solution. It separated from this solution in ill-defined crystals, which, after washing with ether, melted at 160—161°:

0·1426 gave 17·3 c.c. N_2 at 25° and 763 mm. N=13·81.
$C_{18}H_{15}O_2N_3$ requires N=13·76 per cent.

p-Aminomethylformanilide was diazotised and combined with the following phenolic substances: salicylic acid, α-naphthol-4-sulphonic acid (N and W acid), and 8-amino-α-naphthol-3:6-disulphonic acid (H acid), giving rise to a series of azo-dyes, the properties of which are tabulated below.

Azo-derivatives of p-*Aminomethylacylanilides.*

Base.	Phenolic compound.	Colour.	Azo-dye. Dyeing effect on wool (*a*) and silk (*b*).		Colour with concentrated sulphuric acid.
			a.	*b.*	
p-Amino-methyl-form-anilide.	Salicylic acid	orange-brown powder.	brownish-yellow	lemon-yellow	orange-brown
	β-Naphthol	ill-defined dark red nodules			crimson
	"N & W" acid	dark red powder	russet brown	brownish-red	reddish-brown.
	"H" acid	deep purple powder	brownish-purple	"royal" purple	dark brownish-red, crimson on dilution.
p-Amino-methyl-acet-anilide.	Salicylic acid	brownish-yellow powder	greenish-yellow	golden-yellow	bright orange-brown
	β-Naphthol	well-defined red needles			bright crimson
	"N & W" acid	orange-red powder	scarlet	scarlet	reddish-brown
	"H" acid	purple powder	bluish-purple reddened by meta-chrome mordant	"Bordeaux" red	crimson

Acetylmethylaminobenzene-4-azo-β-naphthol,

$$CH_3\cdot CO\cdot N(CH_3)\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH.$$

—This azo-derivative was obtained by grinding together acetylmethylaminobenzene-4-diazohydroxide and β-naphthol; the mixture rapidly turned red and became moist owing to the elimination of water due to the azo-condensation. It was also prepared by diazotising *p*-aminomethylacetanilide in cold concentrated hydrochloric acid, the solution of the soluble diazonium chloride being added to alkaline β-naphthol. The product crystallised from alcohol in well-defined, transparent, red tablets or flattened needles melting at 139°:

0·1414 gave 16·1 c.c. N_2 at 17° and 766 mm. N=13·34.

$C_{20}H_{17}O_2N_3$ requires N=13·15 per cent.

p-Aminomethylacetanilide was also combined with several other phenolic substances, giving rise to the above azo-dyes.

The authors desire to express their thanks to Mr. A. W. H. Upton, A.C.G.F.C., for assistance in the preliminary experiments of this investigation.

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LX.—*The Constitution of Carbamides. Part VII. The Mechanism of the Synthesis of Urea from the Interaction of Carbonyl Chloride and Ammonia. Part VIII. The Formation of Urea and of Biuret from Oxamide*

By EMIL ALPHONSE WERNER and (Part VIII.) GEORGE KINGSFORD CARPENTER.

THE formation of urea from the interaction of carbonyl chloride and ammonia has been generally considered to be a direct change analogous, for example, to the formation of acetamide from the interaction of acetyl chloride and ammonia. For this reason, this synthesis of urea is invariably set forth as 'conclusive' evidence of the 'carbamide' formula. This is mainly due to the fact that the so-called secondary products have been ignored, so far as their bearing on the mechanism of the change is concerned. Given the consideration they deserve, they clearly indicate the true origin of

urea in this reaction, which in truth is no more than Wöhler's synthesis in another form.

Natanson (*Annalen*, 1856, **98**, 287) first isolated urea from this reaction, Regnault (*Ann. Chim. Phys.*, 1838, [ii], **69**, 180) having obtained indications of its formation.

Bouchardat (*Compt. rend.*, 1869, **69**, 961) showed that cyanuric acid and ammelide were formed in addition to urea; Fenton (T., 1879, **35**, 793) suggested that urea was possibly the result of a secondary reaction, on account of the small proportion obtained. Hantzsch and Stuer (*Ber.*, 1905, **38**, 1041, 2326) found cyamelide as an additional product when ammonia was passed into a solution of carbonyl chloride in light petroleum at 0°. This fact is of interest, since it confirms the author's theory of the constitution and polymerisation of cyanic acid (T., 1913, **103**, 1017).

Origin of Urea, and Formation of Biuret in the Interaction of Carbonyl Chloride and Ammonia.

If urea had the 'carbamide' structure, there appears no reason why it should not be formed in quantitative yield without the accompaniment of several secondary products. In view of the evidence, it is remarkable that no explanation of this has yet been suggested.

The cause undoubtedly lies in the recognition of the fact that there exists no tendency to the formation of a compound containing the system $\vdots C(NH_2)_2$, since this cannot form a part of a stable molecule (this vol., p. 624).

It is evident that the formation of cyanuric acid and of cyamelide arises from the polymerisation of cyanic acid ($HOCN \rightleftharpoons HN\vdots CO$), generated according to the scheme:

$$CO{<}^{Cl}_{Cl} + 2NH_3 \longrightarrow \overset{NH_4Cl}{\overset{+}{CO}{<}^{NH_2}_{Cl}} \longrightarrow HCl + \begin{array}{l} HOCN \longrightarrow \text{Cyamelide} \\ \ \ \updownarrow \qquad\qquad\qquad \text{by polymerisation} \\ HN\vdots CO \longrightarrow \text{Cyanuric acid.} \end{array}$$

Cyanic acid being generated in the presence of ammonia, the origin of urea in this synthesis is self-evident. In support of this explanation of the change, it was found that biuret constituted a large part of the secondary products, since it was shown (T., 1913, **103**, 1014, 2278; P., 1914, **30**, 262) that whilst biuret is formed from the union of cyanic acid and urea, ammelide is formed from the interaction of cyanic acid and biuret. It is not surprising that the formation of the latter has been overlooked by previous investigators, since there was no reason to expect its production according to the usual, but incorrect, view of the change.

In order to place on record information as regards the relative proportions of the different products formed, a quantitative study of the reaction at different temperatures has been made.

The following results were obtained after passing a current of dry ammonia into a 3 per cent. solution of carbonyl chloride in benzene until decomposition was completed:

	Expt. I.	Expt. II.	Expt. III.
Temperature	20—25°	40—50°	65—7[illegible]
Products formed	Per cent.	Per cent.	Per cent.
Urea	31·7	37·3	41·2
Biuret	14·4	10·1	7·8
Ammelide.....................	7·65	8·6	10·6
Cyanuric acid	3·45	6·4	5·98
Cyamelide	0·69	trace	none

The results are expressed in proportion to the respective theoretical yields, calculated on the following bases: thus $COCl_2$ = one mol. each of urea, cyanuric acid, and cyamelide, since the two latter are formed from the polymerisation of cyanic acid, $2COCl_2$ = one mol. of biuret, and $3COCl_2$ = one mol. of ammelide.

It will be noticed that in Expts. I and II biuret constitutes the chief product after urea, and whilst the yield falls with rise of temperature, that of ammelide increases, since, in agreement with theory (*loc. cit.*), the formation of the latter from its precursor biuret is promoted at the higher temperature. The conditions being unfavourable for the existence of free cyanic acid, the proportion of cyanuric acid generated was consequently small.

After the crude product from Expt. I had been shaken with a small quantity of pure alcohol, ethyl allophanate (= 5·3 per cent. of the theoretical) was extracted from the benzene–alcohol filtrate. This could only have resulted from a reaction with cyanic acid generated from the substance, $NH_2{\cdot}COCl$, present in the original product, thus, $2NH_2{\cdot}COCl + C_2H_5{\cdot}OH = C_4H_8O_3N_2 + 2HCl$.

Whilst the total chlorine content of the carbonyl chloride was accounted for as ammonium chloride and a small quantity of chloroformamide, it will be seen, from the sum of the other products, taking an average for the three experiments, that only about 62 per cent. of the carbonyl group was recovered. The deficiency was due to decomposition of carbonyl chloride by water generated simultaneously with the formation of ammelide, thus:

$$HN{<}{\begin{matrix}CO{\cdot}NH_2\\CO{\cdot}NH_2\end{matrix}} + OC{:}NH \longrightarrow HN{<}{\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}}{>}C{:}NH + H_2O.$$

When ammonia dissolved in benzene was added to an excess of carbonyl chloride in the same solvent (ratio, $COCl_2 + 2NH_3$), the yield of urea was equal to only 4·6 per cent. of the theoretical. Cyamelide and cyanuric acid were formed in appreciable amount;

biuret and ammelide were absent. Whilst much carbonyl chloride was unchanged, the solution contained 19 per cent. of the theoretical yield of the compound, $NH_2\cdot COCl$ (Expt. IV).

Bouchardat's (*loc. cit.*) conclusion that guanidine was formed in this reaction could not be confirmed.

In support of the author's contention as regards the system $\dot{:}C(NH_2)_2$, and in confirmation of the present theory of the formation of urea in this reaction, it may be pointed out that thiourea is not formed from the interaction of ammonia and thiocarbonyl chloride. The fact that ammonium thiocyanate is produced instead supplies a convincing argument.

Experimental.

The following method was adopted in obtaining the results given under Expts. I, II, and III: 12 grams of carbonyl chloride dissolved in 400 c.c. of freshly distilled benzene were placed in a stout, wide-mouthed bottle provided with a cork which carried a delivery tube, thermometer, and exit tube. A slow current of dry ammonia (generated as described later) was delivered on to the surface of the liquid, which was kept continually agitated. On account of the rather gelatinous form of the product, it was scarcely possible to ensure uniformity in the progress of the reaction or to maintain a constant temperature. In Expt. I, the vessel was immersed in water at 0°, in Expt. II in water at 15°, in Expt. III no artificial cooling was used. The higher temperature given represents the maximum attained during the progress of each experiment.

The details of Expt. I will suffice to illustrate how the different products were estimated.

The solid material, after being washed with benzene, was collected, dried, and extracted with warm alcohol; the residue 12·04 grams of ammonium chloride present), on treatment with water, left 0·436 gram of insoluble matter, from which 0·4 gram of ammelide was extracted by solution in sodium hydroxide. Hence cyamelide present = 0·036 gram. The alcoholic extract was concentrated by evaporation to a small volume; 2·25 grams of crystalline matter (*A*) separated after cooling, and the mother liquor on evaporation to dryness left a residue (*B*) = 2·45 grams.

Product (*A*) contained 0·96 gram of ammonium chloride and 0·95 gram of urea; cyanuric acid was absent, and the remainder (0·34 gram) was chiefly ethyl allophanate with a trace of biuret. Product (*B*) was dissolved in 50 c.c. of water. Cyanuric acid was estimated in an aliquot portion by titration with $N/10$-sodium

hydroxide, using phenolphthalein as indicator: required for total, 14 c.c. $N/10$-NaOH = 0·18 gram $C_3H_3O_3N_3$.

Biuret was estimated colorimetrically, as previously described (T., 1913, **103**, 2282). Found, 0·897 gram; it was also separated in crystalline form and identified (m. p. 192°).

Urea was estimated in this solution by precipitation as nitrate, which was washed with ether, dried, and weighed.

Urea found = 1·36. Hence total urea $(A)+(B) = 2{\cdot}31$ grams = 31·7 per cent. of the theoretical amount from 12 grams of carbonyl chloride.

Since guanidine can be detected with ease, even in a 0·1 per cent. solution and in the presence of urea, and of biuret by means of picric acid, its absence was proved by the negative result obtained with this reagent.

Expt. IV.—Interaction of Carbonyl Chloride and Two Molecular Proportions of Ammonia.—To 4 grams of carbonyl chloride in 100 c.c. of benzene, 0·68 gram of ammonia dissolved in 200 c.c. of benzene was added.

The precipitated material was washed with benzene, collected, dried, and extracted with alcohol. The amount of urea found in the resulting solution, after removal of ammonium chloride, was 0·0278 gram = 4·6 per cent. of the theoretical. The benzene filtrate was shaken with a slight excess of pure sodium hydroxide solution, to which, after neutralisation, an excess of silver nitrate was added. The washed precipitate of silver chloride and silver cyanate was digested with dilute nitric acid to remove the latter salt. The resulting solution required, for precipitation of the silver, 76·8 c.c. of $N/10$-potassium thiocyanate, equal to 19 per cent. of the theoretical amount of the compound, $NH_2{\cdot}COCl$, present in the benzene solution; thus $NH_2{\cdot}COCl + 2NaOH = NaOCN + NaCl + 2H_2O$.

Note on a Convenient Method for obtaining a Continuous Current of Dry Ammonia without the Application of Heat.

The following method has given admirable results, and it seemed worth while to place it on record. It is adaptable to any scale, and where, for example, it was required to saturate 8 litres of alcohol with dry ammonia, the procedure was as follows.

Ammonia solution (D 0·880) was allowed to drop from a separating funnel at a regulated rate on 400 grams of commercial sodium hydroxide, in coarse powder, contained in a round-bottomed flask of about 4 litres capacity. The gas was rapidly liberated,

and the temperature of the mixture gradually fell to nearly zero. The process required no attention beyond occasionally replenishing the supply of ammonia solution; nearly 90 per cent. of the ammonia from 1500 c.c. of the concentrated solution was obtained without any application of heat. In order to avoid interference with the continuity of the process through the effects of back pressure, it was necessary to connect the limb of the separating funnel with a short length of glass tubing drawn out to an aperture of about 0·5 mm., whereby the necessary hydrostatic pressure was maintained.

Summary.

(1) The synthesis of urea from the interaction of carbonyl chloride and ammonia does not supply evidence in support of the 'carbamide' formula.

(2) A quantitative study of the interaction, and the nature and number of the secondary products, has shown that urea is produced from the union of ammonia and cyanic acid (in the keto-form), generated from the decomposition of the compound, $H_2N \cdot COCl$, produced in the first instance.

(3) It is shown, for the first time, that biuret is a product of this reaction.

Part VIII.—The Formation of Urea and of Biuret from Oxamide. [With GEORGE KINGSFORD CARPENTER.]

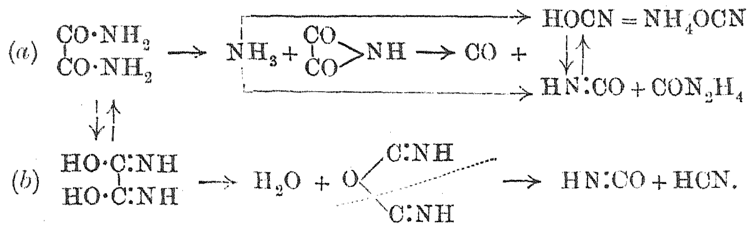
Many years ago, Williamson (*Memoir, Congrès. Scientif. de Venise*, 1847 *) obtained urea by heating a mixture of oxamide and mercuric oxide. This has been accepted as evidence of a close connexion in constitution between urea and the diamide, the latter being supposed merely to lose a carbonyl group in the change.

An investigation of the mechanism of the formation of urea has shown, as expected, that mercuric oxide plays no part in its production; thus, when mixtures of oxamide and mercuric oxide in different proportions were heated to the temperature (230—240°) at which the oxide was completely reduced, no urea could be detected in the product (Expt. I).

When oxamide was heated to a temperature just sufficient to effect complete volatilisation, ammonium cyanate, urea, and biuret were found in the sublimate, whilst ammonia, water, carbon monoxide, and hydrogen cyanide were evolved.

* It was not possible to consult the original paper.

The decomposition is brought about as follows:



Since ammonia was first evolved (at about 110°) whether mercuric oxide was present or not, it is evident that the formation of urea from oxamide, in accordance with (*a*), is but another example of Wöhler's synthesis.

The respective yields of ammonium cyanate and of urea were 2·9 and 4·18 per cent. of the theoretical when oxamide was rapidly heated and the vapours quickly condensed by artificial cooling. When the amide was slowly heated without further precaution, the yields were 2·4 and 2·6 per cent. respectively, whilst the formation of hydrogen cyanide was more evident than in the former case (Expts. II, III, IV, and V). The formation of biuret is accounted for by the above explanation of the mechanism of the decomposition.

It may be mentioned that when *s*-dimethyloxamide was heated with mercuric oxide to 240°, no dimethylurea was formed; when the amide was heated alone, whilst the greater part volatilised unchanged, there was decomposition, represented by the scheme:

$$\begin{array}{l} CO{\cdot}NHMe \\ | \\ CO{\cdot}NHMe \end{array} \longrightarrow NH_2Me + \begin{array}{l} CO \\ | \\ CO \end{array}\!\!>NMe \longrightarrow CO_2 + MeNC.$$

This change is being further investigated.

EXPERIMENTAL.

Expt. I.—An intimate mixture of 1·76 grams of oxamide and 4·32 grams of mercuric oxide was heated in a test-tube partly immersed in glycerol. Ammonia was evolved at 110°, and at 230—240° the colour of the mixture changed to grey and the heating was stopped. The cold residue was extracted with 10 c.c. of water, but no urea could be detected in the solution, even by means of the extremely delicate xanthhydrol test. The experiment was repeated, with different proportions of the two substances, with a similar result.

Expt. II.—Two grams of oxamide were heated in a hard glass tube held horizontally until the whole had sublimed. The sublimate

was extracted with cold water, and to the solution 10 c.c. of N/10-silver nitrate were added, 5·65 c.c. being required for the precipitation of the ammonium cyanate present, which was therefore equal to 2·49 per cent.

Expt. III.—The above experiment was repeated, but the forepart of the tube was cooled with a circular current of water; 6·8 c.c. of N/10-silver nitrate were required; hence 2·9 per cent. of the theoretical amount of ammonium cyanate was present.

Expts. IV and V.—Two grams of oxamide were heated as in Expt. II, the aqueous extract, after removal of 'cyanate,' being evaporated to dryness. The urea extracted by alcohol from the residue gave 6·66 c.c. N_2 at N.T.P. on decomposition with alkaline sodium hypobromite = 2·61 per cent. of the theoretical; 10·68 c.c. N_2 at N.T.P. were obtained from the urea produced under the conditions of Expt. III, which corresponds with 4·18 per cent. of the theoretical amount.

Summary.

(1) Urea is not formed when a mixture of oxamide and mercuric oxide is heated to the stage at which the oxide is completely reduced.

(2) The synthesis of urea from oxamide is the result of the generation of cyanic acid and ammonia from the decomposition of the amide.

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[*Received, July* 18*th*, 1918.]

LXI.—*A New Method for the Determination of Conductivity.*

By EDGAR NEWBERY.

THE convenience and simplicity of Kohlrausch's method for the determination of the conductivity of aqueous solutions has been so long recognised that at the present time no trustworthy data on this subject exist which have not been obtained by the above method or some slight modification of it.

Further, all conductivity vessels are standardised with the aid of the original values given by Kohlrausch for potassium chloride solutions.

A critical examination of the method shows, however, that it is

based on several assumptions which have not so far been experimentally proved correct. The following are the chief objections to the method.

(1) It is assumed that by using alternating current, all polarisation effects are eliminated.

Taylor and Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2396 *et seq.*) have studied this subject, and have shown that consistent results with simple electrolytes can only be obtained by using a perfect sine wave current and extrapolating the results thus obtained to determine the conductivity when the frequency is infinite. It appears probable, therefore, that with these precautions polarisation is absent in the case of simple electrolytes, such as potassium chloride, but when certain other electrolytes are used, especially with insufficiently platinised electrodes, it is by no means certain that decomposition of the electrolyte, with consequent polarisation of the electrodes, does not occur. To quote an extreme case, an alternating current passed between copper electrodes in a concentrated solution of potassium cyanide dissolves the copper with the same efficiency as direct current when the frequency is not greater than 1000 per minute, and with an efficiency of 33 per cent. when the frequency is 38,000 per minute. Since very small traces of polarisation may exert very great influence on the measured conductivity, it follows that grave doubt is thrown on the trustworthiness of many of our present conductivity data.

(2) It is assumed that conductivity is independent of current density, current concentration, and type of current (direct or alternating). Whilst this is probably true in general, it has not been sufficiently investigated to be relied on in all cases.

(3) Errors are introduced by self-induction, electrostatic capacity, shape of conductivity vessel, etc., the corrections for which are troublesome and of doubtful accuracy.

It is therefore very desirable to devise a method of measuring conductivity which will utilise direct current and completely eliminate the effect of polarisation at the electrodes.

EXPERIMENTAL.

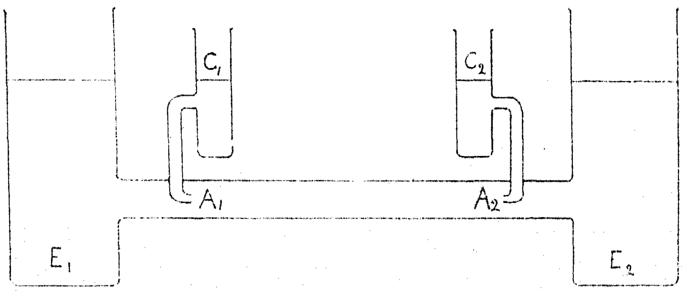
The method described is a simple modification of a common method for measuring the resistance of a metallic conductor by determining the fall of potential along it during the passage of a known current.

Altogether, seven different forms of the apparatus were constructed, but the principle of them all may be seen from Fig. 1, which shows the most convenient form for general use in obtain-

ing relative values, and Fig. 2, which shows the most accurate form for the determination of absolute values.

In using the first form of apparatus, a small but constant current is passed between the electrodes E_1E_2, along the tube A_1A_2, and also through a standard resistance. Standard electrodes (calomel, mercurous sulphate, etc.) are constructed in the vessels C_1C_2, and these are connected with an accurate dial potentiometer reading to five significant figures. The extremities of the standard resistance are also connected to the same potentiometer, and by means of a commutator, the fall of potential along the tube A_1A_2 and across the terminals of the standard resistance may be measured

FIG. 1.



in rapid succession. The specific conductivity of the electrolyte is then given by

$$K = \frac{D^2}{VR} \times \frac{y}{x},$$

where D is the distance between the electrode tips A_1A_2, V the volume of the liquid in the tube between the same points, R the standard resistance, and x and y the potential differences between the electrodes C_1C_2 and between the terminals of the standard resistance respectively. All measurements described were carried out with the apparatus immersed in a thermostat at 25°.

Conductivity of N-*Potassium Chloride at* 25°.

For this purpose, the apparatus shown in Fig. 2 was used. A burette (50 c.c.) was chosen out of a large number such that the graduations were as uniform as possible, and carefully calibrated by a weighing method with mercury, the exact distance between the first and last markings being determined with the cathetometer. (These measurements were repeated after construction of the apparatus.) The tap was then cut off, standard electrode

E E* 2

vessels were sealed on as shown, with the tips central and exactly opposite the end graduations, and large side-tubes, B_1B_2, sealed on well behind the electrode tips. These side-tubes were connected with the main electrode vessels E_1E_2.

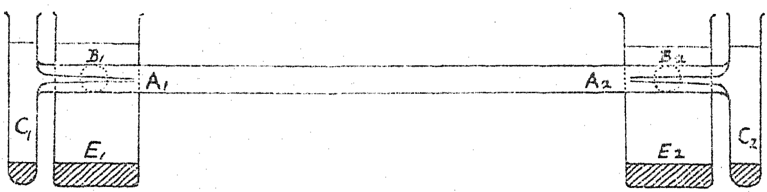
Errors due to expansion of the glass, irregularities in the tube, etc., were calculated and found to amount to not more than 0·001 per cent.

The electrodes used in all four vessels were calomel, great care being taken to secure purity of mercury and calomel. Before use, the electrodes C_1C_2 were connected through a sensitive galvanometer. If any deflexion was observed, they were short-circuited for some time until no difference of potential could be detected.

The main electrode vessels were 8 cm. high and 5 cm. in diameter, the mouths being closed with well-fitting corks to prevent evaporation.

The standard resistance, 99·84 ohms, and the thermometer used were calibrated at the National Physical Laboratory. The

FIG. 2.



galvanometer was a moving coil instrument sensitive to 10^{-9} ampere.

By varying the strength of the main current between 0·1 and 5 milliamperes, readings were taken on very varied portions of the potentiometer.

By repeatedly changing the direction of the main current, errors due to concentration changes in the electrolyte and inequality of potential between C_1 and C_2 were eliminated. By experiments with other forms of the apparatus, using different lengths of tube and different sized electrode tips, it was found that errors due to uneven flow of current in the immediate neighbourhood of the electrode tips are not greater than 0·01 per cent. if the diameter of these tips is not more than 0·1 of that of the main tube.

The chief difficulty experienced in all these experiments lay in securing a perfectly constant main current. The use of calomel electrodes of large area and small currents was so far successful in this case in overcoming this difficulty that long series of closely agreeing results were easily obtained. Other devices for the same purpose are described later.

Purification of Materials.—The water was redistilled, using a tin condenser, and had a conductivity of $0{\cdot}5 \times 10^{-6}$ mhos.

The mercury was redistilled and sprayed through dilute nitric acid several times before use.

The calomel was washed with water and well triturated with mercury and potassium chloride solution several times before being placed in the apparatus.

The potassium chloride was a special product, guaranteed pure by the manufacturers. This was precipitated from a saturated solution by means of hydrogen chloride, dried, and heated to dull redness, and again precipitated from a hot saturated solution in conductivity water by rapid cooling. After drying and heating to dull redness, it was weighed out and the solution made up at 18° to the strength used by Kohlrausch (74·59 grams per litre at 18°). This solution was made up, *ab initio*, three times, starting with different samples of the original salt, and no difference in conductivity could be detected in the three solutions.

The solution was exactly neutral to indicators, and no trace of sulphate, carbonate, phosphate, or nitrate could be detected by the usual tests. Quartz vessels were used wherever possible in the preparation of the salt, and all glass vessels were well steamed out shortly before use to avoid the introduction of sodium silicate. The flame spectrum showed the sodium lines somewhat feebly, but no other ingredient. Since the presence of as much as 1 per cent. of sodium chloride in the potassium salt would only raise the conductivity of the solution by 0·05 per cent., it is improbable that any appreciable error exists due to impurity of the original salt.

Results.—The readings were generally taken in sets of ten, the potential fall along the tube and the standard resistance being taken in alternate order to compensate for slight changes in the main current. After reversal of the current, another set of ten pairs of readings was taken. The current was then broken and the apparatus left for a few hours before repeating the observations. The whole was then cleaned out, dried, and refilled with fresh solution.

Of 100 results thus obtained for the specific conductivity of *N*-potassium chloride, 20 gave the value 0·1126 mho., 29 gave the value 0·1125 mho., and 51 gave 0·1124 mho. at 25°.

The average value is therefore 0·11247 mho., which is higher than that given by Kohlrausch by 0·6 per cent. Since the current used by Kohlrausch was obtained from a small induction coil, which does not give a symmetrical alternating current, polarisation effects were probably present, and his result is probably too low. It is

unlikely that the error in the present work exceeds 0·1 per cent., and 0·1125 is therefore nearer the true value than 0·1118.

Sodium Chloride Saturated at 25°.—Similar precautions were taken to secure purity of materials as in the case of potassium chloride.

The solution was made by shaking excess of the pure salt with conductivity water at 60° for fifteen minutes, and allowing to remain with occasional shaking for twenty-four hours in a thermostat at 25°. Calomel electrodes were used as before.

The final value obtained was 0·2520(5), which is greater than that given by Kohlrausch by 0·3 per cent.

N-*Silver Nitrate* (169·89 *grams per litre at* 18°).—The main electrodes in this case were plates of pure assay silver, "1000 quality." Secondary electrodes of the same material were tried, but were not so satisfactory as calomel electrodes with a connecting liquid of *N*-potassium nitrate.

The value obtained for the specific conductivity was 0·07796 mho. at 25°.

The value calculated from that of Kohlrausch and Steinwehr (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 587) by means of the temperature coefficients given by Déguisne (*Diss.*, Strassburg, 1895) is 0·0779 mho. at 25°.

N-*Sulphuric Acid* (49·043 *grams per litre at* 18°).—The purest available materials were used, and the acid was estimated gravimetrically by precipitation with barium chloride and volumetrically by titration with sodium carbonate.

Mercurous sulphate electrodes were used for both primary and secondary electrodes, and were found to be satisfactory only if used within twenty-four hours of making up. After this time, the mercurous salt gradually dissolves in the acid, increasing its conductivity by 0·1 per cent. in three days, and still more on longer keeping. This raises doubts as to the trustworthiness of the mercurous sulphate electrode for prolonged investigations. No change could be detected within the first twenty-four hours.

The value obtained for the specific conductivity was 0·2137 mho. at 25°.

Kohlrausch gives the value 0·1980 mho. and Loomis (*Ann. Phys. Chem.*, 1897, [iii], **60**, 547) gives 0·195 mho., both at 18°. Using Gotrian's data for temperature coefficient (*Ann. Phys. Chem.*, 1874, [ii], **151**, 378), these give the values 0·2220 and 0·2186 respectively at 25°, which exceed the value found here by 3·6 and 2·2 per cent. respectively.

Summary.

A form of conductivity apparatus is described in which direct current is used and disturbing effects of polarisation at the electrodes are eliminated.

The following values have been obtained for the specific conductivity of solutions in mhos. at 25°:

N-Potassium chloride (74·59 grams per litre at 18°), 0·1124(7).

Sodium chloride saturated at 25°, 0·2520(5).

N-Silver nitrate (169·89 grams per litre at 18°), 0·07796.

N-Sulphuric acid (49·043 grams per litre at 18°), 0·2137.

In conclusion, the author wishes to thank Prof. A. Lapworth for his interest in this work.

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[*Received, May* 31*st*, 1918.]

LXII.—*The Abnormality of Strong Electrolytes. Part III. The Osmotic Pressure of Salt Solutions and Equilibrium between Electrolytes.*

By JNANENDRA CHANDRA GHOSH.

IN the previous papers (this vol., pp. 449, 627) it has been shown that the number of free ions in a given solution containing a gram-molecule of salt is

$$n \, . \, N \, . \, e^{-\frac{A}{nRT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is Avogadro's number, n is the number of ions into which a molecule dissociates, and A is the work required to separate the component ions of a gram-molecule to an infinite distance apart at that particular dilution. It has also been established that only these free ions take part in the conduction of electricity through solutions.

An equation of state free from any arbitrary assumption was deduced by Clausius (*Phil. Mag.*, 1870, [iv], **40**, 122; Jeans, "Dynamical Theory of Gases," 2nd edition, pp. 141—145) from purely dynamical principles, which takes into account the forces of molecular attraction. His theorem $PV = \frac{2}{3}$ kinetic energy $-$ $\frac{1}{3}$ virial is specially suitable for application to salt solutions, since

the work necessary to overcome the forces of electrical attraction in this case can be easily calculated. Milner (*Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 747) has already developed a method for calculating the virial of solutions of univalent binary electrolytes, and has shown that the Clausius theorem agrees well with experimental results. No relation between the activity coefficient $\frac{\mu_v}{\mu_\infty}$ and the osmotic pressure of salt solutions has, however, yet been established on the basis of complete ionisation at all dilutions. We have seen that the molecular conductivity is proportional to the number of free ions, $n.N.e^{-\frac{A}{nRT}}$. Since at infinite dilution $A=0$,

$$\frac{\mu_v}{\mu_\infty}=e^{-\frac{A}{nRT}},$$

or

$$A=nRT\log_e\frac{\mu_\infty}{\mu_v}\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(2)$$

which holds good for all types of salt solutions. Here A, of course, is the virial, and PV thus becomes equal to

$$nRT-\tfrac{1}{3}nRT\log_e\frac{\mu_\infty}{\mu_v},$$

$$=nRT\left\{1-\tfrac{1}{3}\log_e\frac{1}{a}\right\},$$

or

$$i=n.\left\{1-\tfrac{1}{3}\log_e\frac{1}{a}\right\}\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(3)$$

According to Arrhenius, on the view that in a solution we have an equilibrium between ions and undissociated molecules,

$$i=1+(n-1)a\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(4)$$

At infinite dilution, equations (3) and (4) lead to the same limiting value of $i=n$. At other dilutions, the two equations give different results. In this paper it is proposed to examine which of these equations agrees best with actual observations.

Determination of a for Univalent Binary Electrolytes at Various Dilutions.

It has already been shown that the variation of activity-coefficient with dilution for univalent binary electrolytes is given by the equation

$$\frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt[3]{V}}=2RT\log_e\frac{\mu_\infty}{\mu_v}=2RT\log_e\frac{1}{a}.$$

The agreement with the observed values is quite satisfactory for dilutions of 10 litres and upwards (Part I). This coincidence becomes, however, less perfect as the concentration increases. This is certainly due to the fact, suggested by Washburn (*J. Amer. Chem. Soc.*, 1911, **33**, 1464), and later emphasised by Noyes and Falk (*ibid.*, 1912, **34**, 458), that the ratio $\frac{\mu_v}{\mu_\infty}$ is not a true measure of the activity-coefficient. A correction for change in ionic mobility, due to the change in the viscosity of solutions with dilution, is necessary; the ratio $\frac{\mu_v \eta_v}{\mu_\infty \eta_\infty}$, furnishes a much closer approximation to the true values of the activity-coefficient than the ratio $\frac{\mu_v}{\mu_\infty}$. Taking into account this correction for viscosity, the equation for univalent binary electrolytes becomes

$$A = \frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty \eta_\infty}{\mu_v \eta_v} = 2RT \log_e \frac{1}{a}. \quad (5)$$

From table I it will be evident that, with this modification, the above equation can be very well applied to concentrations up to $0{\cdot}5N$. In the table, the values of μ_v and η_v have been taken from the paper of Noyes and Falk (*loc. cit.*). The striking regularity brought to notice by these investigators, that salts of analogous constitution have the same activity-coefficient at the same dilution, is, of course, a necessary deduction of the above equation. Above $0{\cdot}5N$, the volume actually occupied by the solute molecules is not negligible.

TABLE I. T=18°.

Salt.	Extra-polation value of $\mu_\infty \eta_\infty$.	Calc. value of $\mu_\infty \eta_\infty$ from $\mu_{10}\eta_{10}$.		$v=$ 2.	5.	10.	20.
1. NaCl	108·9	109·8	$\mu_v\eta_v$ calc.	82·3	88·8	92·7	96·1
			$\mu_v\eta_v$ obs.	84·2	89·1	92·7	96·1
2. KCl	130·0	132·5	$\mu_v\eta_v$ calc.	99·2	107·0	111·8	115·8
			$\mu_v\eta_v$ obs.	101·3	107·5	111·8	115·6
3. LiCl	98·8	99·0	$\mu_v\eta_v$ calc.	74·2	80·0	83·6	86·7
			$\mu_v\eta_v$ obs.	75·5	80·2	83·6	86·6
4. KBr	132·2	134·5	$\mu_v\eta_v$ calc.	101·0	108·6	113·5	117·6
			$\mu_v\eta_v$ obs.	101·3	109·1	113·5	117·4
5. KI	131·2	133·8	$\mu_v\eta_v$ calc.	100·1	—	112·9	116·9
			$\mu_v\eta_v$ obs.	101·4	—	112·9	116·7

It will be observed that the difference between the calculated value of μ_∞ and the extrapolation value, obtained by means of empirical equations, is within 2 per cent.

TABLE II.

	$V=2.$	5.	10.	20.	50.	100.
Theoretical value of α for all univalent binary electrolytes according to equation 5. Per cent.......	74·8	80·8	84·4	87·5	90·6	92·4

Variation of α with Dilution for Ternary Electrolytes.

For ternary electrolytes, the variation of activity-coefficient with dilution is very satisfactorily represented by the equation

$$\frac{6N \,.\, E^2 \,.\, \sqrt[3]{2N}}{D \,.\, \sqrt{3} \,.\, \sqrt[3]{V}} = 3RT \log_e \frac{\mu_\infty}{\mu_v} = 3RT \log_e \frac{1}{\alpha}.$$

In table III, the percentage values of α, calculated from the above equation for various dilutions, are given.

TABLE III.

$v=$	10.	20.	40.	50.	100
$\alpha=$	67·8	73·5	78·3	79·7	84·0

Determination of the Value of i for Univalent Binary Electrolytes.

The method of determining i with sufficient exactness is based on observations on the lowering of the freezing point of salt solutions. Attempts were made to determine i from the diminution of the vapour pressure of solutions (compare Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 231), but until the recent work of Lovelace, Frazer, and Miller (*J. Amer. Chem. Soc.*, 1916, **38**, 515) the methods were not sufficiently accurate. These investigators have succeeded in improving the technique of the method to such an extent that the temperature of the bath can be kept constant within 0·001° for more than twelve hours, and a pressure of 0·0001 mm. can be exactly measured. The results obtained by them are rather peculiar, inasmuch as the molecular lowering of the vapour pressure of a solution of potassium chloride remains constant as the concentration changes from $2N$ to $0{\cdot}2N$. Any opinion on these results must at present be suspended, as the work is still in progress.

The method based on the lowering of the freezing point has been well investigated, and all the observations, with the exception of those of Ponsot (*Ann. Chim. Phys.*, 1897, [vii], **10**, 79; 1899, **16**, 162), go to show that i continually increases until the limiting

value n is reached. Noyes and Falk, in their valuable paper on the properties of salt solutions (*J. Amer. Chem. Soc.*, 1910, **32**, 1020), have given a fairly complete account of the investigations on the lowering of the freezing point up to that time. They have not attached the same weight to the data obtained by different investigators, and hence their mean value of i is somewhat arbitrary. In table IV I have recalculated the mean value of the molecular lowering of the freezing point on the simpler, but still arbitrary, basis that the probable error of the various investigators is approximately the same. The value of i is obtained by dividing the mean molecular lowering of the freezing point by 1·858. In the footnote are given the references to the work of the investigators whose data have been utilised in calculating the mean value of i.

The weighted mean of the "molecular number i" for salts of the uni-univalent type, obtained by Noyes and Falk (*loc. cit.*, p. 1027), is included in table VIII for the sake of comparison. It should be noted that this mean was obtained by excluding the data on the molecular numbers of lithium chloride and sodium bromide. The values of i for these salts, as will be seen from table IV, are always higher than the mean. For ternary electrolytes, Noyes and Falk do not give any weighted mean, but observe that "the values of the molecular numbers are of similar magnitude, the range being 2·57 to 2·68 at dilution 10 and 2·71 to 2·77 at dilution 50."

TABLE IV.

Salt.	$V=2$.	5.	10.	20.	50.	100.
KCl[1]	1·800	1·833	1·862	1·886	1·922	1·947
NaCl[2]	1·824	1·850	1·880	1·897	1·928	1·945
LiCl[3]	—	—	1·901	1·912	1·928	1·937
CsCl[4]	1·780	—	1·878	1·892	1·930	—
NaBr[5]	—	1·871	1·891	1·911	—	—
KBr[6]	1·813	1·841	1·870	1·910	1·929	—

[1] Jones, *Zeitsch. physikal. Chem.*, 1893, **11**, 110; **12**, 639. Loomis, *Ann. Phys. Chem.*, 1894, [iii], **51**, 500; 1896, **57**, 495; 1897, **60**, 523; *Zeitsch. physikal. Chem.*, 1900, **32**, 578; 1901, **37**, 406. Lewis, *ibid.*, 1894, **15**, 365. Abegg and Nernst, *ibid.*, 1894, **15**, 681; 1896, **20**, 207. Whetham, *ibid.*, 1900, **33**, 344. Raoult, *ibid.*, 1898, **27**, 617. Jahn, *ibid.*, 1905, **50**, 129; 1907, **59**, 31. Richards, *ibid.*, 1903, **44**, 563. Ponsot, *loc. cit.* Bedford, *Proc. Roy. Soc.*, 1910, [*A*], **83**, 454.

[2] Jones, Loomis, Raoult, Ponsot, Abegg, Jahn, Hausrath, *Ann. Physik*, 1902, [iv], **9**, 522. Osaka, *Zeitsch. physikal. Chem.*, 1902, **41**, 560.

[3] Loomis, Jahn.

[4] Jahn, Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 185.

[5] Jahn.

[6] Jahn, Biltz.

TABLE V.

Mean value of i for univalent binary electrolytes at various dilutions.

$v=$	2.	5.	10.	20.	50.	100.
$i=$	1·805	1·849	1·880	1·900	1·935	1·942

Determination of i *for Ternary Electrolytes at Various Dilutions.*

In calculating the value of i, the method described before has been followed. Table VI contains the mean value of i for some well-investigated ternary electrolytes at various dilutions.

TABLE VI.

Salt.	Mean value of i.	$v = 10$.	20.	50.
$CaCl_2$[1]	i =	2·624	2·685	2·789
$MgCl_2$[2]	i =	2·677	2·708	2·763
$SrCl_2$[3]	i =	2·629	2·673	2·781
$BaCl_2$[4]	i =	2·580	2·640	2·712
$ZnCl_2$[5]	i =	2·579	2·666	2·771
$CO(NO_3)$[6] ...	i =	2·700	2·760	—
$Cu(NO_3)$[7] ...	i =	2·630	2·730	—
$Ni(NO_3)_2$[8] ...	i =	2·600	2·670	2·810

[1] Loomis, Ponsot, Jones and Pearce. [2] Loomis. [3] Loomis, Jones and Pearce. [4] Bedford, Loomis, Jones, Ponsot, Whetham. [5] Jones. [6] Jones and Pearce. [7] Jones and Pearce. [8] Jones and Pearce.

TABLE VII.

Mean value of i for ternary electrolytes at various dilutions.

$v=$	10.	20.	50.
$i=$	2·620	2·691	2·771

The Validity of the Clausius Theorem.

TABLE VIII.

	$v=$ 2.	5.	10.	20.	50.	100.
i According to Noyes and Falk	1·804	1·837	1·865	1·887	1·925	1·937
i Observed for univalent binary salts	1·805	1·849	1·880	1·900	1·935	1·942
i According to equation 3	1·806	1·859	1·887	1·910	1·934	1·947
i According to equation 4	1·748	1·808	1·844	1·875	1·906	1·924

TABLE IX.

	$v=$10.	20.	50.
i Observed for ternary salts.........	2·620	2·691	2·771
i According to equation 3............	2·616	2·695	2·773
i According to equation 4............	2·356	2·470	2·594

It is evident that the equation

$$i = n\left\{1 - \tfrac{1}{3}\log_e \frac{\mu_\infty}{\mu_v}\right\},$$

based on the Clausius theorem, agrees best with the experimental results. The Arrhenius equation fails conspicuously in the case of ternary electrolytes. Jones attempted to explain this anomaly by his hydrate theory. The high value of i according to him, is due to the fact that the solvent combines with the solute, the ratio of solute to solvent molecules increases, and hence i becomes abnormally large. His theory may be correct for concentrated solutions. There is, however, some inherent improbability in the fact that in dilute solutions about 150 water molecules must be made to combine with an ion in order that the difference between the observed value of i and that calculated from Arrhenius's equation may be explained. The hydrate theory of dilute solutions becomes simply unnecessary in view of the complete validity of the Clausius theorem as applied to salt solutions.

Activity-coefficient of Salts in Mixed Solutions.

Here we have the following empirical rule: "The conductivity and the freezing-point lowering of a mixture of salts having one ion in common are those calculated under the assumption that the degree of ionisation (activity-coefficient) of each salt is that which it would have if it were present alone at such an equivalent concentration, that the concentration of either of its ions is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture" (A. A. Noyes, *Tech. Quart.*, 1904, **17**, 301).

Let there be two solutions of sodium chloride and potassium chloride, and let their equivalent dilutions be V and V' respectively. If X and Y are their respective activity-coefficients, then

$$\log\frac{1}{x} = k\left(\frac{1}{V}\right)^{\frac{1}{3}},$$

and

$$\log\frac{1}{y} = k\left(\frac{1}{V'}\right)^{\frac{1}{3}}.$$

If the two solutions are mixed together, the total volume $= V + V'$. But, on mixing, there is a distribution of arrangement until the entire solution is uniform. Since there are only ions in a solution, and since the arrangement in sodium chloride and potassium chloride solutions is identical, the distance between the sodium and chlorine ions in an electric doublet is the same as it would have

been if the dilution were $\frac{V+V'}{1+1}$. The result is that the activity-coefficient of sodium chloride in the mixture corresponds with that of the pure solution at dilution $\frac{V+V'}{2}$, which is the equivalent dilution of the common ion. The same is true for potassium chloride. On mixing, therefore,

$$\log \frac{1}{x'} = k\left(\frac{2}{V+V'}\right)^{\frac{1}{3}},$$

$$\log \frac{1}{y'} = k\left(\frac{2}{V+V'}\right)^{\frac{1}{3}}.$$

where x' and y' are the respective activity-coefficients of the salts in the mixture.

Therefore $X'=Y'$, or the activity-coefficient of each of the salts is the same and corresponds with that of a solution the equivalent concentration of which is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture.

If $V=V'$, that is, if the initial concentration of both solutions is the same,

$$\frac{1}{V} = \frac{1}{V'} = \frac{1+1}{V+V'},$$

therefore $X=Y=X'=Y'$. That is, the activity-coefficient does not change when two salt solutions having the same equivalent concentration are mixed. This is the condition for isohydry.

Conclusions.

In this series of papers on the abnormality of strong electrolytes, I have proceeded on the following assumptions:

(1) A salt solution is always completely ionised, the force of attraction between ions being governed by the law of inverse squares.

(2) The arrangement of ions in a univalent binary electrolyte corresponds with a simple cubic lattice, whilst in a solution of a ternary electrolyte the arrangement corresponds with a fluorspar lattice.

The following equations have been derived:

I. $A = \frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v}$ . . . for universal binary salts.

II. $A = \frac{6N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} = 3RT \log_e \frac{\mu_\infty}{\mu_v}$ . . . for ternary salts.

III. $i = n \left\{1 - \frac{1}{3} \log_e \frac{\mu_\infty}{\mu_v}\right\}$

The validity of these fundamental equations has been completely demonstrated both in aqueous and non-aqueous solutions. The variation of the activity-coefficient with temperature has been successfully calculated, and the conditions for isohydry have been determined. In fact, a complete theory of dilute salt solutions has been propounded.

My best thanks are due to Prof. P. C. Rây and to my friend and colleague Mr. J. N. Mukherjee, M.Sc.

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LXIII.—*The Preparation of certain Organic Stanno- and Stanni-chlorides.*

By JOHN GERALD FREDERICK DRUCE.

DOUBLE haloids of tin with organic bases have long been known. Thus Cook (*Amer. Chem. J.*, 1899, **22**, 435) described a number of aliphatic amine salts, and Slagle (*ibid.*, 1898, **20**, 633) prepared the aniline and toluidine compounds. Pyridine stannochloride has been described by Hayes (*J. Amer. Chem. Soc.*, 1902, **24**, 360), and pyridine stannichloride by Weinland and Bames (*Zeitsch. anorg. Chem.*, 1909, **62**, 250). The quinoline salts have been isolated by Borsbach (*Ber.*, 1890, **23**, 431).

These salts were usually prepared from hydrochloric acid solutions of the component haloids, and the same method of preparation has been employed in the case of the new compounds described below.

EXPERIMENTAL.

Diethylamine Stannochloride, $(NHEt_2)_2,H_2SnCl_4$.—This salt was isolated from a dilute hydrochloric acid solution containing two molecular proportions of amine to one of stannous chloride. The crystals which separated were collected and dried on a porous plate in a desiccator over sodium hydroxide. The salt was very deliquescent and melted at 58°:

0·9852 gave 0·3640 SnO_2. Sn = 29·11.
0·5950 ,, 0·8355 AgCl. Cl = 34·75.
$(C_4H_{11}N)_2,H_2SnCl_4$ requires Sn = 29·04; Cl = 34·69 per cent.

o-*Toluidine Stannochloride*, $(C_7H_7 \cdot NH_2)_2,H_2SnCl_4$.—*o*-Toluidine (5·35 grams) was added to 100 c.c. of a dilute hydrochloric acid solution containing 5·65 grams of stannous chloride, and warmed. On cooling, fine, silky needles, melting at 164°, were deposited.

The salt dissolved readily in cold water, the solution remaining clear unless boiled:

0·4385 gave 0·1382 SnO_2. Sn = 24·82.
0·1205 ,, 0·1454 AgCl. Cl = 29·85.
$(C_7H_9N)_2,H_2SnCl_4$ requires Sn = 24·90; Cl = 29·75 per cent.

o-*Toluidine Stannichloride*, $(C_7H_9N)_2,H_2SnCl_6,H_2O$.—This compound was obtained in very pale pink, short needles, which began to decompose at 210°:

0·8247 gave 0·2274 SnO_2. Sn = 21·23.
0·1228 ,, 0·1841 AgCl. Cl = 37·39.
$(C_7H_9N)_2,H_2SnCl_6,H_2O$ requires Sn = 21·01; Cl = 37·64 per cent.

Methylaniline Stannochloride, $C_7H_9N,HSnCl_3$.—Redistilled methylaniline (5·35 grams) and stannous chloride (5·65 grams) were dissolved together in 100 c.c. of hot dilute hydrochloric acid. The clear solution deposited a mass of short, stout, colourless prisms dissolving in water to a clear solution, which became turbid only on boiling. The salt is also soluble in alcohol, but not in chloroform, and melts at 106°:

0·2549 gave 0·1157 SnO_2. Sn = 35·75.
0·3264 ,, 0·4224 AgCl. Cl = 32·02.
$C_7H_9N,HSnCl_3$ requires Sn = 35·63; Cl = 31·93 per cent.

Methylaniline Stannichloride, $(C_7H_9N)_2,H_2SnCl_6$.—Molecular proportions of the base and hydrated crystalline stannic chloride were dissolved together in dilute hydrochloric acid. Colourless crystals of the stannichloride, melting and decomposing at 251°, separated from the solution. The salt dissolved in water to a clear solution, which was not appreciably hydrolysed even when boiled:

0·5054 gave 0·1401 SnO_2. Sn = 21·78.
0·1728 ,, 0·2703 AgCl. Cl = 38·71.
$(C_7H_9N)_2,H_2SnCl_6$ requires Sn = 21·67; Cl = 38·84 per cent.

Chlorination of a dilute hydrochloric acid solution of the stannochloride also gave this compound, but the product was not pure and had a low melting point.

m-*Phenylenediamine Stannochloride*, $C_6H_4(NH_2)_2,2HSnCl_3$.—This compound was obtained by reducing *m*-nitroaniline or *m*-dinitrobenzene with tin and hydrochloric acid. It forms fine, silky prisms, melting at 128°, which are soluble in water, but the

solution soon becomes cloudy. Dilute hydrochloric acid solutions of the salt gave the reactions for stannochlorides, for example, iodine solutions were decolorised; a white precipitate was obtained with mercuric chloride solution, which darkened on warming, and a dark brown precipitate of stannous sulphide was obtained by passing in hydrogen sulphide:

0·4211 gave 0·2232 SnO_2. Sn = 41·75.
0·4537 „ 0·6891 AgCl. Cl = 37·58.
$C_6H_8N_2,2HSnCl_3$ requires Sn = 41·85; Cl = 37·97 per cent.

m-*Phenylenediamine Stannichloride*, $C_6H_8N_2,H_2SnCl_6$.—Dilute hydrochloric acid solutions of the above stannochloride were oxidised to stannochloride on exposure to air, but the crystals isolated from these solutions were not pure. The pure salt was obtained from *m*-nitroaniline (2·56 grams) or from *m*-dinitrobenzene (1·3 grams) and stannous chloride (10·5 grams). Almost colourless crystals of the stannichloride separated from the hydrochloric acid solution. It dissolved readily in cold water, and the solution did not hydrolyse unless heated. The crystals melted and decomposed at 265°:

0·4762 gave 0·1606 SnO_2. Sn = 26·56.
0·4511 „ 0·8767 AgCl. Cl = 48·07.
$C_6H_8N_2,H_2SnCl_6$ requires Sn = 26·88; Cl = 48·18 per cent.

No double haloids of *o*-phenylenediamine could be prepared.

p-*Phenylenediamine Stannochloride*, $C_6H_8N_2,H_2SnCl_4$.—This salt was obtained as a mass of compact, opaque, white crystals readily soluble in water. The solution was easily hydrolysed by gently warming. The crystals melted and decomposed at 270°:

0·5547 gave 0·2246 SnO_2. Sn = 31·90.
0·5547 „ 0·8436 AgCl. Cl = 37·63.
$C_6H_8N_2,H_2SnCl_4$ requires Sn = 32·06; Cl = 38·26 per cent.

p-*Phenylenediamine Stannichloride*, $C_6H_8N_2,H_2SnCl_6$.—Oxidation of solutions of the stannochloride gave impure stannichloride. A pure specimen was obtained by treating *p*-nitroaniline with a molecular proportion of stannous chloride in hydrochloric acid. The nacreous plates dissolved in cold water without appreciable hydrolysis, but, on boiling, a precipitate was formed. The salt melted and decomposed at 230°:

0·3784 gave 0·1282 SnO_2. Sn = 26·69.
0·1180 „ 0·2305 AgCl. Cl = 48·32.
$C_6H_8N_2,H_2SnCl_6$ requires Sn = 26·88; Cl = 48·18 per cent.

Benzylamine Stannochloride, $C_6H_5·CH_2·NH_2,HSnCl_3$.—This salt was obtained by warming together benzonitrile (5 grams) and tin

(12 grams) in 50 c.c. of concentrated hydrochloric acid diluted with 20 c.c. of water under a reflux condenser for three hours. On cooling, a mass of short, silky crystals was deposited, which gave the usual reactions for stannochlorides, and softened at 95° and decomposed at about 210°:

0·4491 gave 0·2045 SnO_2. Sn = 35·70.
0·2864 ,, 0·3592 AgCl. Cl = 31·03.
$C_7H_9N,HSnCl_3$ requires Sn = 35·63; Cl = 31·93 per cent.

Benzylamine Stannichloride, $(C_7H_9N)_2,H_2SnCl_6$.—Benzonitrile (2·06 grams) was heated with stannous chloride (9·04 grams) in hydrochloric acid, with shaking, under a reflux condenser until a clear solution was obtained. From this, soft, shining crystals separated in flakes resembling naphthalene and melting at 112°:

0·3465 gave 0·0943 SnO_2. Sn = 21·51.
0·3465 ,, 0·5421 AgCl. Cl = 38·83.
$(C_7H_9N)_2,H_2SnCl_6$ requires Sn = 21·85; Cl = 38·84 per cent.

p-*Methylbenzylamine Stannochloride*,
$CH_3{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2,HSnCl_3$.
—Ten grams of tin and 5 grams of *p*-toluonitrile were heated with hydrochloric acid as in the case of the benzylamine salt, which this compound also resembled in properties. Both dissolved slowly in water, and the solutions soon decomposed. On heating, it melted at 107°:

0·5248 gave 0·2290 SnO_2. Sn = 34·38.
$C_8H_{11}N,HSnCl_3$ requires Sn = 34·29 per cent.

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[*Received, July 19th, 1918.*]

LXIV.—*The Basic Carbonates of Copper.*

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IN connexion with an investigation of the composition of a cellulose cuprammonium–hydroxide solution made by dissolving cotton-wool in a solution of commercial copper carbonate in ammonium hydroxide, one of the authors had occasion to examine a number of samples of commercial "copper carbonate."

Pickering (T., 1909, **95**, 1410) states that the ordinary copper carbonate of commerce has the formula $2CuO,CO_2,H_2O$, identical

with malachite. The present paper does not support that statement.

According to some text-books, also, the compound precipitated when sodium carbonate is added to a solution of copper carbonate in the cold has the composition $2CuO,CO_2,2H_2O$, which changes to $2CuO,CO_2,H_2O$ on keeping.

The amount of copper oxide in thirteen different samples of commercial copper carbonate from different European and Indian sources is shown in table I. The percentages of copper oxide theoretically found in the basic carbonates of copper, for which a definite composition is claimed, are also quoted for purposes of comparison and reference.

TABLE I.

Percentage of Copper Oxide found in Thirteen Samples of Commercial Copper Carbonate.

1	2	3	4	5	6	7	8	9	10	11	12	13
78·60	71·71	71·52	69·69	69·58	69·55	69·29	68·90	68·61	68·41	68·36	67·84	66·16

Small quantities of impurity were present, usually iron, but in no case was the amount sufficient to account for the widely different results.

Name of Compound.	CuO per cent.	CO_2 per cent.	H_2O per cent.
Pickering's compound (*loc. cit.*), $8CuO,3CO_2,6H_2O$ ...	72·62	15·06	12·32
Malachite, $CuCO_3,Cu(OH)_2$ or $2CuO,CO_2,H_2O$	71·94	19·95	8·11
Azurite, $2CuCO_3,Cu(OH)_2$ or $3CuO,2CO_2,H_2O$	69·23	25·54	5·22
$CuCO_3,Cu(OH)_2,H_2O$ or $2CuO,CO_2,2H_2O$...	66·53	18·41	15·06

Assuming that the commercial copper carbonates have the composition of malachite, it was thought that the adsorption of moisture on exposure to the atmosphere might account for the low results found. In order to test this, copper carbonate, in the form of a fine powder and spread in thin layers, was first dried in a steam-oven at 97° for more than three hours, and then, after weighing, was exposed to the atmosphere of the laboratory for three days (15—17°) and weighed at intervals. The amount of increase in weight fluctuated during this time, but the maximum increase recorded amounted to 1·06 per cent. This would not account for the variations in copper oxide content shown in table I.

If the copper oxide content is any indication of the composition of the compound, it would appear that the commercial compound more nearly approximates to the composition of azurite. In order to obtain further evidence on this point, five samples were examined

which contained from 69·55 to 71·71 per cent. of copper oxide. The same samples contained from 17·35 to 18·1 per cent. of carbon dioxide. Comparison with the above table will show that these results are much below those required for malachite or azurite. It appears from this that the statement that commercial copper carbonate has the same composition as malachite is incorrect, and that in reality the substance is a mixture of very varying composition.

The authors of the present paper made various attempts to prepare a basic carbonate of copper of approximately constant composition in a simple manner, as it was desired to devise a process which could be used by comparatively inexperienced workers. Table II shows the methods employed and the percentages of copper oxide obtained.

TABLE II.

Method.	CuO per cent.
Copper sulphate solution precipitated in the cold with cold sodium carbonate solution	71·82
Copper sulphate solution (hot) precipitated with cold sodium carbonate solution	78·85
Copper sulphate solution (cold) precipitated with cold saturated solution of sodium hydrogen carbonate	77·09
Copper sulphate solution (cold) precipitated with cold 5 per cent. sodium hydrogen carbonate solution	71·08
Boiling saturated copper sulphate solution precipitated with cold saturated sodium hydrogen carbonate solution. The burner was removed before the addition of the sodium hydrogen carbonate	72·37

In all cases, the precipitates were washed free from sulphate.

These results yielded no valuable prospects, and it was decided to see if the desired result could be achieved by taking solutions of known strength. In the earlier experiments (from which tables I and II are compiled), the carbonates were carefully heated in a crucible, the residue being cooled in a desiccator and weighed. The heating, etc., was repeated until a constant weight was obtained. This method presents several defects, and it was decided to make complete analyses of the substances produced. This was done by heating a weighed amount of the substance in a boat contained in a short, lead-glass tube, the water and carbon dioxide being collected by means of the usual absorption apparatus employed in organic combustions. All heating was done by means of Bunsen burners manipulated by hand, and the experiment was carried out in an atmosphere of dry oxygen.

It was observed that in one or two cases the copper oxide was distinctly crystalline in appearance. In all the other cases, the

copper oxide was very dark brown, not black. Tests performed on the oxide showed it to be free from impurity.

A saturated solution of purified copper sulphate (14·5°) was diluted with an equal volume of distilled water, and to the cold solution was added a cold (14·5°) solution of pure sodium carbonate (10 per cent.). The precipitate was allowed to remain for twenty-four hours, and then washed on a Büchner funnel with distilled water until free from sulphate. The precipitate, on solution, contained no sulphate. It was dried in a steam-oven at 96° until its weight was constant.

TABLE III.

	CuO per cent.	CO_2 per cent.	H_2O per cent.	Total per cent.
The average composition of the precipitate was	72·98	15·46	11·89	100·33
$13CuO,5CO_2,9H_2O$ requires	73·02	15·54	11·44	100·00
Pickering's compound $8CuO,3CO_2,6H_2O$ requires	72·62	15·06	12·32	100·00

The above percentages give the formula: $13{\cdot}07CuO,5CO_2,9{\cdot}40H_2O$.

The Basic Carbonate, $2CuCO_3,5Cu(OH)_2$ *or* $7CuO,2CO_2,5H_2O$.

A solution of pure copper sulphate, saturated at 14·5°, was diluted with an equal quantity of distilled water, and to this solution was added a solution containing 5 per cent. of sodium carbonate and 5 per cent. of sodium hydrogen carbonate. The carbonate solution was added with stirring until, on filtering a small portion, the filtrate gave no precipitate with it. The mixture was allowed to remain until next day, and was then filtered on a Büchner funnel and washed free from sulphate. This required

TABLE IV.

No.	CuO per cent.	CO_2 per. cent.	H_2O per cent.	Total per cent.
(*a*) Mean of three analyses	75·90	11·25	12·78	99·93
(*b*) Mean of four analyses	75·48	11·55	13·18	100·21
(*c*) Mean of three analyses	75·39	12·04	12·88	100·31
Mean	75·59	11·61	12·95	100·15
$2CuCO_3,5Cu(OH)_2$ requires	75·77	11·98	12·25	100·00

Stated as formulæ the above results become :—

(*a*) $7CuO,1{\cdot}89CO_2,5{\cdot}20H_2O$.
(*b*) $7CuO,1{\cdot}93CO_2,5{\cdot}39H_2O$.
(*c*) $7CuO,2{\cdot}01CO_2,5{\cdot}28H_2O$.
Mean: $7CuO,1{\cdot}94CO_2,5{\cdot}29H_2O$.
Theory: $7CuO,2{\cdot}00CO_2,5{\cdot}00H_2O$.

many hours, and usually extended until the next morning. The wet precipitate was then allowed to remain until the third day and dried in a steam-oven. The drying process never lasted less than six hours.

Three separate preparations, (*a*), (*b*), and (*c*), were made. The analyses of these preparations are shown in table IV (p. 721).

Summary.

Examination of a number of samples of commercial copper carbonate gave evidence to show that the statement that it has the same composition as malachite is erroneous.

An attempt has been made to prepare a basic copper carbonate of approximately constant composition from pure materials.

A new basic copper carbonate, $2CuCO_3,5Cu(OH)_2$ or

$$7CuO,2CO_2,5H_2O,$$

is described.

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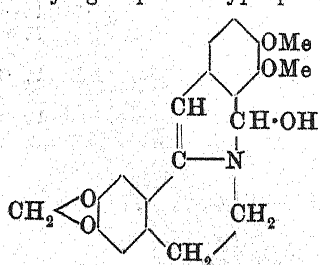
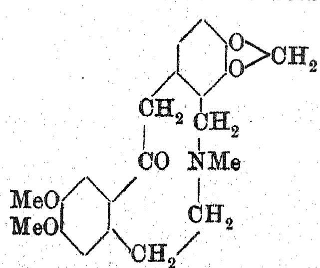
LXV.—*A Study of some Derivatives of Berberine Closely Allied to Derivatives of Cryptopine.*

By WILLIAM HENRY PERKIN, jun.

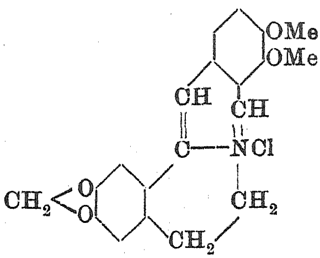
THE close relationship which exists between berberine and cryptopine has been discussed on more than one occasion (compare T., 1916, **109**, 833, 841; this vol., p. 493), and it has been pointed out that, if the formulæ of the alkaloids, or better still of their quaternary salts, are written side by side, it is readily seen that the difference between the two is, in the main, the presence of the *N*-methyl group in cryptopine and its absence in the berberine



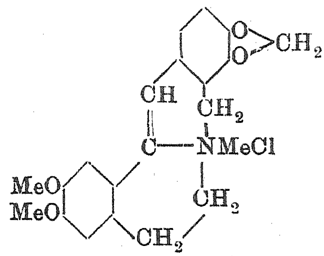
Berberine.



Cryptopine.

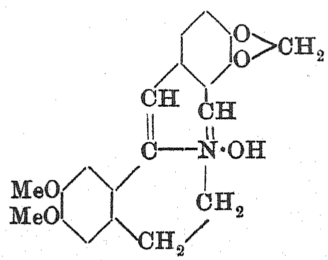


Berberinium chloride.



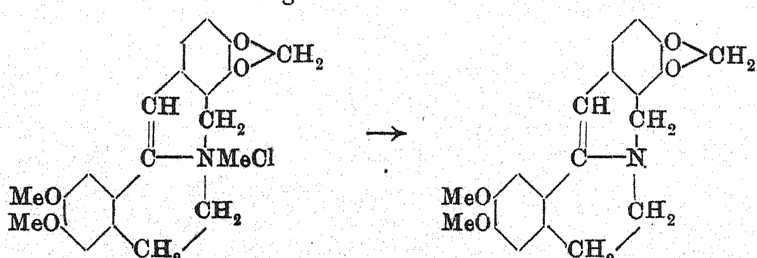
*iso*Cryptopine chloride.

molecule, and the fact that the positions of the two methoxy-groups and the methylenedioxy-group are reversed in the two formulæ. It was further pointed out that the alkaloid of the berberine type which actually corresponds with cryptopine is *epi*berberinium hydroxide,



*epi*Berberinium hydroxide.

and the conversion of cryptopine into this interesting alkaloid has recently been described (this vol., p. 493). The problem which had to be solved in attempting the preparation of *epi*berberine from cryptopine was essentially the discovery of some method which would render possible the removal of the *N*-methyl group from the latter alkaloid, and this difficult step was ultimately accomplished by heating *iso*cryptopine chloride at 280°, when methyl chloride was eliminated according to the scheme:

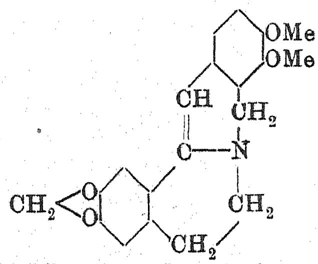


*iso*Cryptopine chloride. Dihydroanhydro*epi*berberine.

The dihydroanhydro*epi*berberine obtained in this way served as the principal source from which a considerable number of derivatives of *epi*berberine were subsequently obtained and examined.

The object of the present investigation was to accomplish the reverse change, namely, to introduce an *N*-methyl group into the berberine molecule in order to study derivatives of berberine which were similarly constituted to corresponding derivatives of cryptopine, and only differed from these in containing the two methoxy-groups and the methylenedioxy-group in the reversed positions. It was hoped that results might be obtained in this way that would confirm and amplify certain curious observations made during the study of the derivatives of cryptopine, and this has proved to be the case.

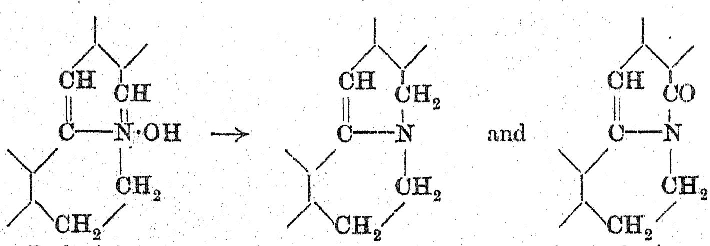
The substance most largely employed for the purposes of this investigation has been dihydroanhydroberberine,*



Dihydroanhydroberberine.

and the opportunity was taken to bring forward additional evidence in support of the identity and constitution of this important substance.

Dihydroanhydroberberine was first obtained by Gadamer (*Arch. Pharm.*, 1905, **243**, 35) during the course of a valuable investigation into the action of alkalis on berberinium hydroxide. Gadamer showed that berberinium sulphate or hydroxide, when heated on the steam-bath with concentrated sodium hydroxide solution, undergoes simultaneous reduction and oxidation with the formation of dihydroanhydroberberine and oxyberberine:



Berberinium hydroxide. Dihydroanhydro-berberine. Oxyberberine.

* With regard to the nomenclature employed in this communication for berberine and its derivatives, compare this vol., p. 503.

According to Gadamer, dihydroanhydroberberine melts at 165—167°, crystallises in deep yellowish-brown tablets, yields a hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$, and is readily oxidised on exposure to the air to berberine. At a later date (*Monatsh.*, 1910, **31**, 557), Faltis expressed the opinion that the reaction between berberinium hydroxide and sodium hydroxide was not analogous to the Cannizzaro reaction between aromatic aldehydes and alkali, but was similar to the change which Decker (*Ber.*, 1903, **36**, 2568) has observed to take place when quinoline methiodide is treated with an alkali:

$$3C_9H_7N,MeI + 3NaOH = \underset{\substack{N\text{-Methyl-}\\ \text{quinolone.}}}{2C_9H_6ONMe} + \underset{\substack{N\text{-Methyltetra-}\\ \text{hydroquinoline.}}}{C_9H_{10}NMe} + 3NaI + H_2O.$$

In other words, Faltis was of opinion that the substance which Gadamer had described as dihydro(anhydro)berberine was in reality tetrahydro(anhydro)berberine. That such a suggestion could have been made is remarkable, for, with the exception of almost identical melting points (168—170°), there are scarcely any points of resemblance between dihydroanhydroberberine and tetrahydroanhydroberberine. Tetrahydroanhydroberberine is colourless and gives colourless salts, of which the hydrochloride has the composition $C_{20}H_{21}O_4N,HCl$; dihydroanhydroberberine has a striking, yellowish-brown colour and yields a deep yellow hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$. The mistaken view which Faltis advanced is doubtless partly due to the fact that he used impure dihydroanhydroberberine for his experiments, for he states (*loc. cit.*, p. 567) that the material that he employed melted at 135—155°, whereas pure dihydroanhydroberberine melts at 166—168°.

Faltis further makes the erroneous statement that there is no depression in melting point when equal quantities of dihydroanhydroberberine and tetrahydroanhydroberberine are mixed, whereas the present author finds that such a mixture of the pure substances softens at 140—145°, and is completely melted at 152°. Faltis did not make any comparative analyses of dihydroanhydroberberine and tetrahydroanhydroberberine, or he would have suspected that these substances could not be identical, since the former, $C_{20}H_{19}O_4N$, contains C = 71·2, H = 5·6, whereas the latter, $C_{20}H_{21}O_4N$, contains C = 70·8, H = 6·2, a difference quite easily detected by accurate analysis (compare p. 739). The only positive evidence which Faltis brings forward in support of his view that these bases are identical is that they require approximately equal amounts of iodine to oxidise them to berberine. A method of this kind carried out under the conditions observed by Faltis would be

open to grave suspicion in any case, and is obviously quite valueless when impure material is employed in the determinations.

The contention that dihydroanhydroberberine and tetrahydroanhydroberberine are identical was subsequently dealt with by Gadamer (*Arch. Pharm.*, 1910, **248**, 670), who not only discussed in detail the points raised by Faltis and showed that they are groundless, but also brought forward further and convincing evidence that the substance described by him as dihydro(anhydro)-berberine is in fact that substance.

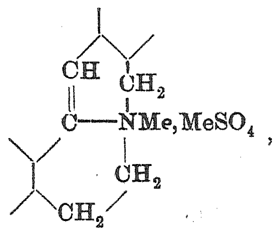
The results of the present investigation indirectly confirm the identity of dihydroanhydroberberine, and additional positive evidence has arisen from the observation that it is possible to grow crystals of this substance and also of tetrahydroanhydroberberine from acetone which are suitable for crystallographical examination. The measurement of these crystals, which was kindly undertaken by Miss M. W. Porter (p. 741), clearly proves that these substances cannot possibly be identical.

In only one point does the experience of the author in connexion with dihydroanhydroberberine differ from the accurate statements of Gadamer. Gadamer frequently mentions that this base and its salts are easily oxidised by exposure to air and converted into berberine and its salts. The present author, on the other hand, cannot confirm this ready oxidisability. A specimen of the pure hydrochloride which had remained on porous porcelain in a drawer exposed to air for more than six months yielded the same analytical results as before exposure, and the solution of a weighed quantity in water gave, on the addition of ammonia, a precipitate of dihydroanhydroberberine which was nearly the amount which should have been obtained from the pure hydrochloride (p. 740). If conversion of the hydrochloride into berberinium chloride had taken place during exposure, there would either have been no precipitate on the addition of ammonia or, in the event of partial change, a diminished yield. Again, a specimen of pure dihydroanhydroberberine which had been several times recrystallised from acetone and melted at 167—168° was left on a watch-glass exposed to the air for six months without apparent change. At the end of this time, the specimen melted at the same temperature as before exposure and yielded the same analytical results, an experience which is in accord with the statement of Gadamer that a specimen of dihydroanhydroberberine, crystallised from ether, which he had prepared in 1902, still showed the same melting point in 1910 as when first prepared. It seems therefore clear that dihydroanhydroberberine is not readily oxidised by contact with air, and this is in harmony with the behaviour observed in the analogous case of

dihydroanhydro*epi*berberine (this vol., p. 507), which also may be exposed to the air for a long time without apparent change.

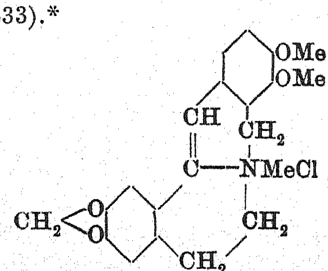
Dihydroanhydroberberine Methosulphate and its Conversion into Anhydromethylberberine.

The basis of the experiments chronicled in the following pages is *dihydroanhydroberberine methosulphate* (p. 743),

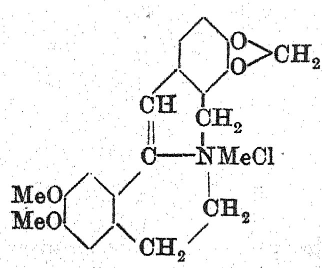


which is readily prepared by the direct combination of dihydroanhydroberberine with methyl sulphate, and separates from methyl alcohol in brilliant yellow, orthorhombic prisms melting at 205°.

The corresponding *methiodide*, $C_{20}H_{19}O_4N,MeI$ (m. p. 215—220°), which is obtained from the methosulphate by precipitation with potassium iodide, had already been described by Freund and Fleischer (*Annalen*, 1915, **409**, 231), who prepared it by the direct addition of methyl iodide to dihydroanhydroberberine. *Dihydroanhydroberberine methochloride*, $C_{20}H_{19}O_4N,MeCl$ (m. p. 223°), obtained by digesting the iodide with water and silver chloride, separates from water, apparently with $5H_2O$, in pale yellow prisms. This methochloride has been made the subject of special inquiry on account of its close relationship to *iso*cryptopine chloride (833).*



Dihydroanhydroberberine methochloride.



*iso*Cryptopine chloride.

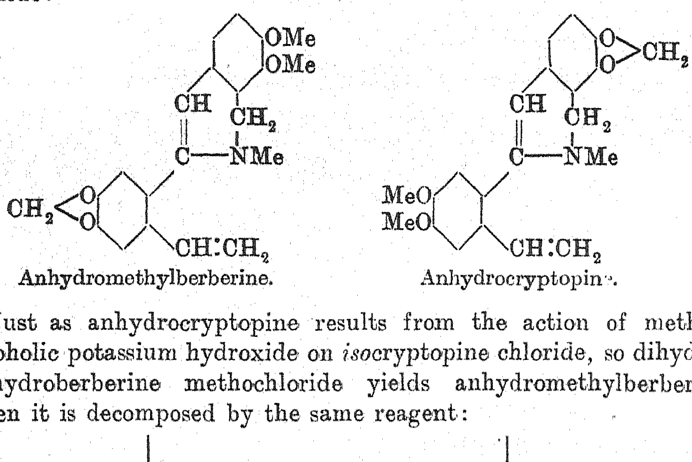
These so closely allied quaternary chlorides exhibit, as was to be expected, great similarity in their properties and reactions. They

* The numbers in brackets—thus (833)—refer to the paper on Cryptopine and Protopine (T., 1916, **109**, 815–1028).

are both characterised by sparing solubility in dilute hydrochloric acid, although dihydroanhydroberberine methochloride is more readily soluble both in water and dilute hydrochloric acid than *iso*cryptopine chloride.

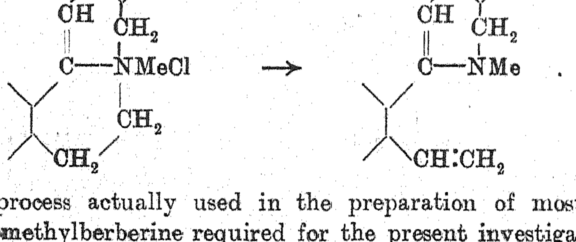
Interesting results have been obtained from the study of the reduction of dihydroanhydroberberine methochloride, and these are described on p. 732. The behaviour of *iso*cryptopine chloride under the same conditions has also been investigated, and will form the subject of a future communication.

Anhydromethylberberine.—This interesting substance corresponds in its method of preparation and in its properties with anhydrocryptopine (850), the relationship between the two substances being at once evident when their formulæ are written side by side:



Anhydromethylberberine. Anhydrocryptopine.

Just as anhydrocryptopine results from the action of methyl-alcoholic potassium hydroxide on *iso*cryptopine chloride, so dihydroanhydroberberine methochloride yields anhydromethylberberine when it is decomposed by the same reagent:

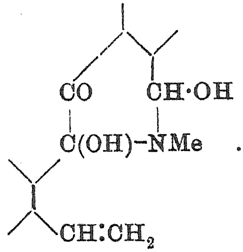


The process actually used in the preparation of most of the anhydromethylberberine required for the present investigation was the direct decomposition of dihydroanhydroberberine methosulphate by boiling with methyl-alcoholic potassium hydroxide (p. 746).

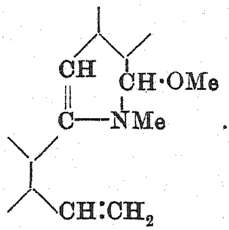
Anhydromethylberberine, $C_{21}H_{21}O_4N$, melts at 94—95° (anhydrocryptopine at 110—111°) and separates from methyl alcohol in pale yellow prisms.

Like anhydrocryptopine, it is a rather weak base, since the

acetate, for example, is dissociated by water, but the salts with mineral acids are stable in the presence of excess of acid. It undergoes a curious change when its solution in methyl alcohol is slowly evaporated in contact with air, yielding, besides a large quantity of a brittle resin, a small amount of a crystalline substance, $C_{21}H_{21}O_7N$ (p. 747), which melts at 153—155°, has no basic properties, and is probably a *trioxyanhydromethylberberine* containing the grouping:

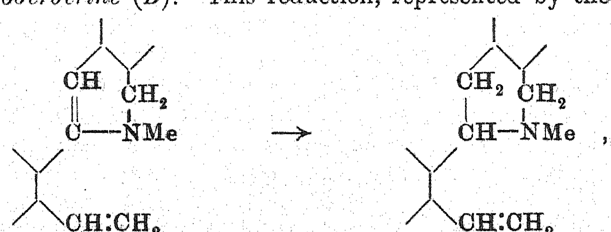


In this respect, anhydromethylberberine appears to behave differently from anhydrocryptopine, since the latter, when boiled with methyl alcohol in contact with air, yields by the addition of methyl alcohol and simultaneous oxidation, large quantities of the two isomeric methoxyanhydrocryptopines (A) and (B) (856), which contain the grouping:



It is, of course, possible that substances corresponding with the two modifications of methoxyanhydrocryptopine are contained in the resin which is the main product of the action of methyl alcohol and air on anhydromethylberberine, but attempts to isolate such substances in a crystalline condition have been unsuccessful.

Reduction of Anhydromethylberberine to N-*Methyl*iso*tetrahydroanhydroberberine* (B).—This reduction, represented by the scheme

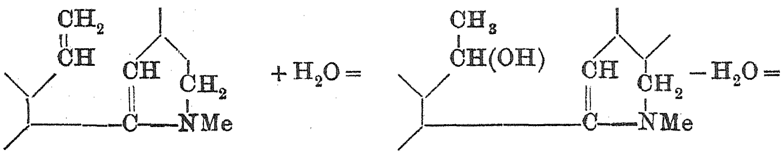


corresponds exactly with the reduction of anhydrocryptopine (989) to anhydrodihydrocryptopine (*B*). The addition of hydrogen takes place readily when the solution of anhydromethylberberine in dilute sulphuric acid is treated with sodium amalgam (p. 748), and, on adding ammonia, a base separates which melts at 112—113° and is identical with *N*-methyl*iso*tetrahydroanhydroberberine (*B*) which Pyman (T., 1913, **103**, 827) obtained from tetrahydroanhydroberberine methohydroxide by evaporation under atmospheric pressure. The similarity in constitution and properties between the anhydrodihydrocryptopines and *N*-methyl*iso*tetrahydroanhydroberberines has already been fully discussed (841), and the preparation of dihydroanhydroberberine methochloride and its conversion first into anhydromethylberberine and then into *N*-methyl*iso*tetrahydroanhydroberberine now completes the picture.

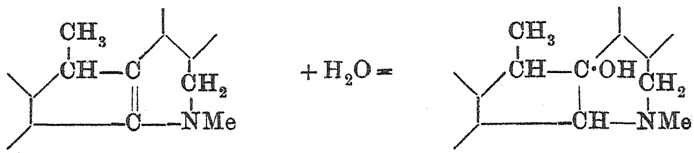
*The Action of Hydrochloric Acid on Anhydromethylberberine. Formation of the Hydroxy*iso*anhydrodihydromethylberberines (A) and (B).*

A highly characteristic property of anhydrocryptopine is the brilliant crimson colour which is produced when this substance is boiled with *concentrated* hydrochloric acid (865), and the same colour is produced in less degree when anhydromethylberberine is treated in the same manner. In the case of the action of concentrated hydrochloric acid on anhydrocryptopine, it was found possible to isolate two crystalline products, namely, the *epi*cryptopines (*A*) and (*B*), but attempts to obtain similar products in a crystalline condition from the product of the interaction of anhydromethylberberine and concentrated hydrochloric acid have been unsuccessful. On the other hand, another reaction, highly characteristic of anhydrocryptopine, namely, its behaviour towards *dilute* hydrochloric acid, is reproduced exactly when anhydromethylberberine is subjected to the action of dilute hydrochloric acid under the same conditions. When anhydrocryptopine is heated with dilute hydrochloric acid (860), it is converted, by the addition of water into the stereoisomeric hydroxy*iso*anhydrodihydrocryptopines (*A*) and (*B*), which melt at 227° and 117° respectively, and the probable course of the reaction and constitution of these substances has already been fully discussed (862). Anhydromethylberberine is very readily acted on by hot *dilute* hydrochloric acid (p. 752), and yields, as the result of the addition of water, two isomeric *hydroxy*iso*anhydrodihydromethylberberines*, (*A*) and (*B*), which melt respectively at 210—212° and 168—170°. Since these

substances behave in all their properties exactly like the hydroxy*iso*anhydrodihydrocryptopines, there can be little doubt that they also are stereoisomeric, and that their formation may be expressed by the scheme:



Anhydromethylberberine.



*iso*Anhydromethylberberine. Hydroxy*iso*anhydrodihydromethylberberine (*A*) and (*B*).

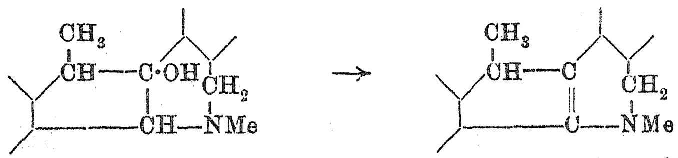
The hydroxy*iso*anhydrodihydromethylberberines (*A*) and (*B*) react very readily with acetyl chloride, and the result of the interaction is the same in either case. The product is a mixture of the hydrochlorides, $C_{21}H_{22}O_5NAc,HCl$, of two acetoxy*iso*anhydrodihydromethylberberines, one of which is more readily soluble than the other. The more sparingly soluble hydrochloride (m. p. 253°) yields, on decomposition with ammonia, the acetyl derivative, $C_{21}H_{22}O_5NAc$, which melts at 165—167°, together with some hydroxy*iso*anhydrodihydromethylberberine (*A*) produced by hydrolysis. It would therefore appear that the substance melting at 165—167° is *acetoxy*iso*anhydrodihydromethylberberine* (*A*).

The more readily soluble hydrochloride gives, with ammonia, an acetyl base, $C_{21}H_{22}O_5NAc$, which melts at 213—215°, and is presumably *acetoxy*iso*anhydrodihydromethylberberine* (*B*). It is, however, difficult to be certain as to the identity of these acetyl derivatives, since, on boiling with dilute hydrochloric acid, both yield a mixture of the two hydroxy*iso*anhydrodihydromethylberberines (*A*) and (*B*).

iso*Anhydromethylberberine.*

In connexion with the investigation of the hydroxy*iso*anhydrodihydrocryptopines (*A*) and (*B*) (861), it was pointed out that one of the most characteristic properties of these stereoisomerides is the conversion into *iso*anhydrocryptopine (m. p. 158—160°), a change which both undergo when they are boiled with concentrated

hydrochloric acid or digested with phosphoryl chloride. The (*A*) and (*B*) modifications of hydroxy*iso*anhydrodihydromethylberberine behave in an exactly similar manner (p. 756) and yield *iso*anhydromethylberberine, $C_{21}H_{21}O_4N$, which, like the corresponding cryptopine derivative, crystallises beautifully in glistening prisms and melts at 123—124°. The formation of this substance from the hydroxy*iso*anhydrodihydromethylberberines is due to dehydration, and the change is probably correctly represented thus:



Hydroxy*iso*anhydrodihydromethylberberine. *iso*Anhydromethylberberine.

iso*Anhydromethylberberine* yields well-defined, sparingly soluble salts, of which the hydrochloride, $C_{21}H_{21}O_4N,HCl$ (m. p. 205—210°), and the hydriodide, $C_{21}H_{21}O_4N,HI$ (m. p. 247°), were prepared and analysed.

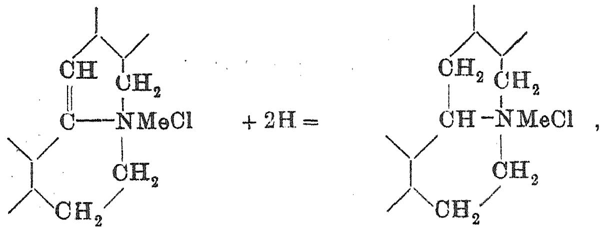
When the sulphate is boiled with excess of dilute sulphuric acid, hydration occurs, and two substances, $C_{21}H_{23}O_5N$, are produced which melt at 215° and 165—167° respectively.

These consist of the (*A*) and (*B*) modifications of hydroxy*iso*anhydrodihydromethylberberine, and the production of these modifications, in this manner, is strong evidence that the view of their formation from anhydromethylberberine advanced on p. 731 is correct.

Reduction of Dihydroanhydroberberine Methochloride.

The interesting behaviour of dihydroanhydroberberine methochloride on reduction in boiling dilute hydrochloric acid solution with sodium amalgam has been made the subject of an extended investigation (p. 758), partly with the view of comparing the results with those obtained from the study of the reduction of *iso*cryptopine chloride under the same conditions, an investigation which it is hoped will form the subject of a future communication. Under the conditions mentioned, dihydroanhydroberberine methochloride yields a quaternary chloride (*a*) and the hydrochloride (*b*) of a new base. The quaternary chloride (*a*), produced by the addition of two atoms of hydrogen to the double linking, can be separated by fractional crystallisation into two substances melting at 245—250° and 280—285° respectively, and these are identical with

the (α-) and (β-) modifications of the methochloride of tetrahydroanhydroberberine first prepared by Pyman (T., 1913, **103**, 825, 826) by the addition of methyl iodide to tetrahydroanhydroberberine and subsequent treatment with silver chloride. The reduction of dihydroanhydroberberine methochloride in this case has therefore proceeded in a simple manner according to the scheme:

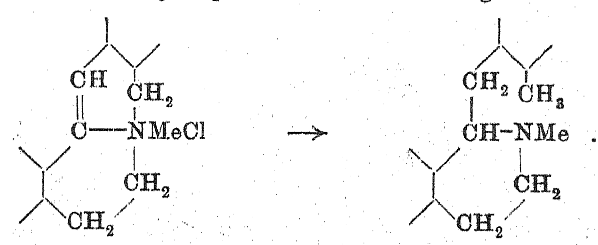


a process which creates an asymmetric carbon atom, and thus allows of the formation of stereoisomeric methochlorides, because the molecule already contains an asymmetric centre, namely, the nitrogen atom attached to five different groups.

The base from the hydrochloride (*b*) is a syrup, has the composition $C_{21}H_{25}O_4N$, and has therefore been produced from dihydroanhydroberberine methochloride according to the equation

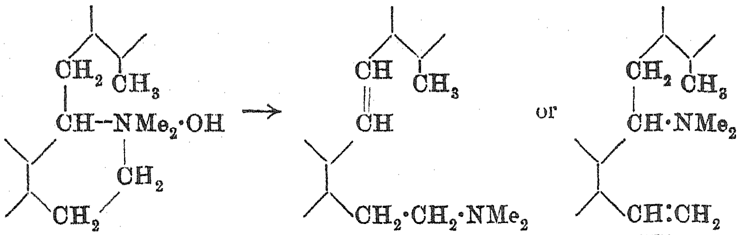
$$C_{20}H_{19}O_4N,MeCl + 7H = C_{20}H_{25}O_4NMe + HCl.$$

The comparison of the properties of this base with those of a similar but better characterised base, which has been obtained by the reduction of *iso*cryptopine chloride, leaves little doubt that its formation is correctly expressed in the following manner:



This base is therefore *dihydromethyl*iso*tetrahydroanhydroberberine* (compare Pyman, T., 1913, **103**, 828). It combines readily with methyl sulphate, and the resulting methosulphate is decomposed by boiling with methyl-alcoholic potassium hydroxide (p. 760), with the formation of *dihydrodimethyl*iso*tetrahydroanhydroberberine*, $C_{22}H_{27}O_4N$ (950). There are two directions in which the elimination of water from the methohydroxide (I) may

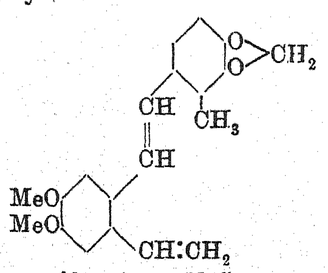
take place, leading to the formation of substances represented by formulæ II or III:



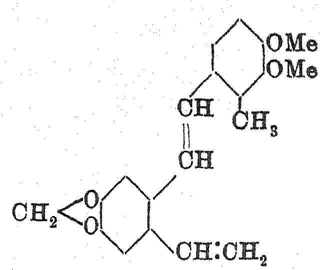
(I.) (II.) (III.)

The mechanism of the change is, in both cases, so similar that there seems no reason why the process should take one direction rather than the other. Arguing, however, again from the analogous behaviour of *iso*cryptopine chloride in the same circumstances—in which case it has been clearly demonstrated that the substance produced by the elimination of water from the methohydroxide corresponding with I has formula II, and not III—there is every reason to suppose that the formula of dihydrodimethyl*iso*tetrahydroanhydroberberine is that represented by II. This syrupy base yields a crystalline methosulphate, $C_{22}H_{27}O_4N,Me_2SO_4$, which, on boiling with methyl-alcoholic potassium hydroxide, readily loses trimethylamine and water and yields a beautifully crystalline substance, $C_{20}H_{20}O_4$, which melts at 113—114°.

Careful investigation of this substance has shown that it is completely analogous to cryptopidene (827), and it has therefore been named '*berberidene*.' The intimate relationship between these two substances is well brought out when their formulæ are written side by side:



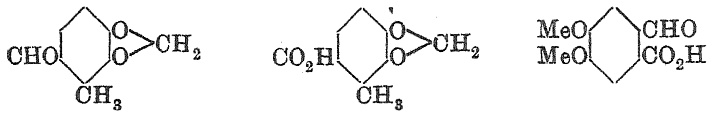
Cryptopidene (m. p. 124°).



Berberidene (m. p. 114°).

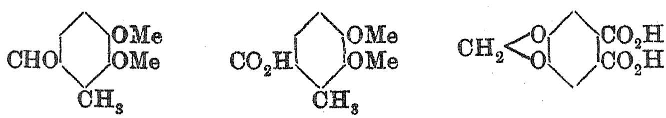
The main evidence in support of the formula assigned to cryptopidene was derived from the study of its behaviour on oxidation, when it yielded 5:6-methylenedioxy-*o*-tolualdehyde (I) and 5:6-methylenedioxy-*o*-toluic acid (II) from the upper part of the mole-

cule and 4:5-dimethoxy-2-aldehydobenzoic acid (*m*-opianic acid, III) from the lower section:



(I.) (II.) (III.)

When berberidene was subjected to oxidation, in acetone solution with permanganate (p. 762) in exactly similar circumstances, it yielded 5 : 6-dimethoxy-*o*-tolualdehyde (IV), 5 : 6-dimethoxy-*o*-toluic acid (V), from the upper, and an acid melting at 174—176°, which was doubtless hydrastic acid (VI), from the lower part of the molecule:

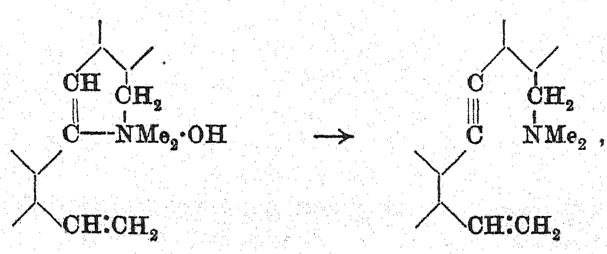


(IV.) (V.) (VI.)

The formation of these substances is obviously in complete harmony with the constitution assigned above to berberidene.

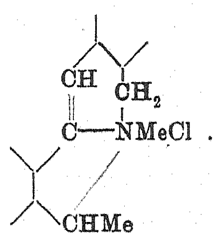
Anhydromethylberberine Methosulphate and ψ-Methylberberinium Chloride.

Anhydrocryptopine combines readily with methyl sulphate, yielding a colourless, crystalline methosulphate (978) which resembles other methosulphates in many of its reactions, but is characterised by the remarkable fact that it is decomposed by alkalis with regeneration of anhydrocryptopine, whereas normally the methyl derivative should have resulted. Attempts to explain the unusual course of this decomposition were made at the time (854), but it was not then pointed out that if the reaction had proceeded normally it would have led to the formation of a substance containing a triple bond, and it is possible that the disinclination to



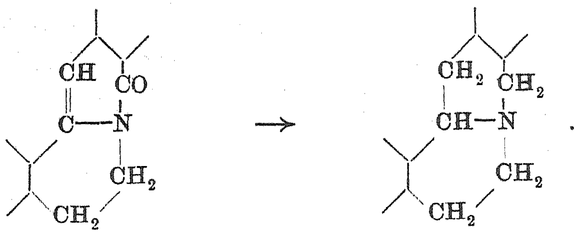
form such a substance may be very great and is perhaps a factor in bringing about the abnormal decomposition of the methosulphate.

In view of the unusual properties exhibited by anhydrocryptopine methosulphate, it was clearly of interest to ascertain whether anhydromethylberberine would yield a methosulphate which would behave in a similar manner. This has been found to be the case. Anhydromethylberberine, $C_{21}H_{21}O_4N$, combines readily with methyl sulphate, and the resulting methosulphate, $C_{21}H_{21}O_4N,Me_2SO_4,H_2O$, crystallises from water in colourless needles melting at 150—152°. The *methiodide*, $C_{21}H_{21}O_4N,MeI$, obtained from the methosulphate by precipitation with potassium iodide, closely resembles anhydrocryptopine methiodide in appearance and general properties, and it is curious that both melt at the same temperature (188—190°). When anhydromethylberberine methosulphate is digested with methyl-alcoholic potassium hydroxide, decomposition occurs readily and a substance separates which, after crystallisation from methyl alcohol, melts at 92—94° and consists of anhydromethylberberine, the yield being almost quantitative. In this decomposition, anhydromethylberberine methosulphate behaves in precisely the same unusual way as anhydrocryptopine methosulphate.

ψ-Methylberberinium Chloride, 

Just as ψ-cryptopine chloride (m. p. 110°) results from the action of boiling concentrated hydrochloric acid on anhydrocryptopine methosulphate (984), so the same process applied to anhydromethylberberine methosulphate leads to the formation of *ψ-methylberberinium chloride*, $C_{21}H_{22}O_4NCl,H_2O$. This interesting quaternary chloride closely resembles ψ-cryptopine chloride in its curious colour reactions and other properties (p. 751). It crystallises well from dilute hydrochloric acid, melts at about 95—100°, and yields, when its aqueous solution is mixed with potassium iodide, *ψ-methylberberinium iodide*, $C_{21}H_{22}O_4NI$, which melts at 175—180°.

Reduction of Oxyberberine to Tetrahydroanhydroberberine,



The synthesis of oxyberberine was accomplished by Pictet and Gams in 1911 (*Compt. rend.*, **152**, 1102), but as these investigators were unable to reduce oxyberberine to tetrahydroanhydroberberine, which, on oxidation in acid solution, would in turn yield salts of berberine, they were obliged to devise another method in order to complete the synthesis of the salts of berberine (*Compt. rend.*, 1911, **153**, 386; *Ber.*, 1911, **44**, 2480). The present author finds, however, that oxyberberine may be readily reduced electrolytically to tetrahydroanhydroberberine under the conditions given on p. 764. It follows, therefore, that the synthesis of oxyberberine by Pictet and Gams is now also a synthesis of berberine

EXPERIMENTAL.

The Action of Sodium Hydroxide on Berberinium Chloride.

Preparation of Oxyberberine and Dihydroanhydroberberine.

The conversion of berberinium sulphate into oxyberberine and dihydroanhydroberberine by heating with sodium hydroxide was first observed by Gadamer (*Arch. Pharm.*, 1905, **243**, 35), and at a later date (*ibid.*, 1910, **248**, 676) more complete details of the process and of the isolation of the products were given by the same investigator. The method recommended is, however, a tedious one and has the disadvantage that the isolation of the products not only entails a large number of operations, but necessitates the use of large volumes of ether.

Since considerable quantities of dihydroanhydroberberine were required for the present research, the author has carried out a series of comparative experiments on the action of sodium hydroxide on berberinium chloride (which is more accessible than the sulphate), and, as the result, the following procedure has been adopted for the preparation of dihydroanhydroberberine and oxyberberine. Commercial berberine hydrochloride (berberinium

chloride, 500 grams) is thoroughly mixed with aqueous sodium hydroxide (700 c.c. of 30 per cent.) in a stout, round-bottomed flask and left for half an hour. The flask is then suspended in a large enamelled basin full of cold water, and the basin slowly heated over a ring burner in such a manner that the water comes to the boil in about half an hour, and it is better not to stir at this stage. The heating is continued for an hour, during which the viscid, dark brown mass may be shaken round repeatedly so as to bring it into better contact with the alkali. On keeping overnight, the black, syrupy layer will have solidified; the aqueous alkali is then run off, the mass washed in the flask with water by decantation, and mixed with dilute hydrochloric acid until the whole is strongly acid. After heating on the steam-bath and filtering by the aid of the pump, the residue is ground up and the treatment with hot dilute hydrochloric acid repeated until all the basic substance has been extracted and a nearly colourless mass of oxyberberine remains.

The different extracts are mixed, while still hot, with concentrated hydrochloric acid, when, on keeping, a large crop of crystals separates which consists of the hydrochloride of dihydroanhydroberberine mixed with varying quantities of unchanged berberinium chloride.

The crops of crystals from the hydrochloric acid extracts, obtained as described above, are collected, washed with dilute hydrochloric acid to remove the dark greenish-brown solution, and recrystallised by dissolving in the least quantity of boiling water and adding concentrated hydrochloric acid. After being collected, the crystals are dissolved in hot water and mixed with excess of ammonia, when a dark brown, semi-solid mass separates which soon hardens. This is ground up and washed by the aid of the pump with hot water until the filtrate is no longer dark purplish-brown;* the residue is then left on porous porcelain until dry. In order to

* The intensely coloured filtrate deposits, on keeping, a splendid chocolate coloured salt which crystallises from hot water in brilliant chocolate coloured needles and was at first thought to be a new substance. In this condition the salt had the remarkable property of dissolving in boiling dilute hydrochloric acid to an orange solution and separating in deep orange needles. Even after repeated recrystallisation from dilute hydrochloric acid, the salt retained the peculiarity of dissolving in boiling dilute ammonia to an intense purple solution from which chocolate coloured needles separated on cooling. However, after repeated crystallisation from methyl alcohol, the salt lost this property and was found to consist of berberinium chloride, since it yielded oxyberberine and dihydroanhydroberberine with sodium hydroxide. The methyl-alcoholic mother liquors contain the highly coloured substance and, when the solution is concentrated, this separates, mixed with berberinium chloride, in almost black needles, the nature of which has not been determined.

purify this crude dihydroanhydroberberine, the best plan is to triturate it with methyl alcohol, in which it is sparingly soluble, then to transfer to the filter and wash with methyl alcohol until the intensely red impurity has been removed, and finally to repeat the same process with acetone. The residue melts at 163—166° and is dihydroanhydroberberine of good quality; after two crystallisations from acetone the substance is quite pure (m. p. 168—170°). The acetone liquors from the washing and crystallisations of the crude dihydroanhydroberberine yield, on concentration, a further crop, which is, however, very dark coloured, and the better plan is to distil off the acetone and dissolve the dark syrup in boiling dilute hydrochloric acid. The solution is mixed with concentrated hydrochloric acid, the hydrochloride which separates on keeping is recrystallised and worked up for dihydroanhydroberberine exactly as already described. Since Faltis (*Monatsh.*, 1910, **31**, 565) has stated that the substance obtained in the decomposition of a berberinium salt with sodium hydroxide is not dihydroanhydroberberine, $C_{20}H_{19}O_4N$, but tetrahydroanhydroberberine, $C_{20}H_{21}O_4N$, three different preparations were analysed:

0·1142 gave 0·2970 CO_2 and 0·0581 H_2O. C=70·9; H=5·6.
0·1075 „ 0·2805 CO_2 „ 0·0550 H_2O. C=71·2; H=5·7.
0·1161 „ 0·3032 CO_2 „ 0·0591 H_2O. C=71·3; H=5·7.
$C_{20}H_{19}O_4N$ requires C=71·2; H=5·6.
$C_{20}H_{21}O_4N$ requires C=70·8; H=6·2 per cent.

Dihydroanhydroberberine melts, according to Gadamer, at 169—170°, and the specimens used in the above analyses all melted when moderately rapidly heated at 168—170°. An intimate mixture of approximately equal amounts of dihydroanhydroberberine and tetrahydroanhydroberberine (m. p. 170°) softened at 140—145° and was completely melted at 152°, so that there can be no question of their identity.

Dihydroanhydroberberine is sparingly soluble in methyl alcohol or acetone, even on boiling, but dissolves more readily in boiling ethyl alcohol. It is rather readily soluble in boiling benzene, from which it crystallises well in yellow prisms. The solution in acetic acid does not give a characteristic coloration on the addition of sulphuric acid, but the addition of a trace of dilute nitric acid causes a deep brown to develop.

In view of the fact that anhydromethylberberine (p. 730) is so readily changed by boiling with hydrochloric acid, and this substance and dihydroanhydroberberine are so similarly constituted it seemed desirable that the behaviour of dihydroanhydroberberine towards hydrochloric acid should also be investi-

gated. The powdered base dissolves readily when mixed with concentrated hydrochloric acid and heated to boiling by means of a sulphuric-acid bath, and the deep yellow solution becomes paler as the boiling continues. After ten minutes, the hydrochloric acid was boiled off, leaving a yellow syrup which, on the addition of water, immediately crystallised in yellow needles, and these consisted of dihydroanhydroberberine hydrochloride. The solution of the salt in warm water gave with ammonia the free base, which, after crystallisation from methyl alcohol, melted at 168° and consisted of dihydroanhydroberberine.

The Stability of Dihydroanhydroberberine and its Salts when exposed to Air.—It is pointed out in the introduction (p. 726) that Gadamer more than once directs attention to the ready oxidisability of dihydroanhydroberberine and its salts when left in contact with air (for example, *Arch. Pharm.*, 1905, **243**, 37; 1910, **248**, 671, 672, 674), and that the present author is unable to confirm this ready oxidisability. The evidence in support of the stability of dihydroanhydroberberine and its hydrochloride towards atmospheric oxygen is as follows: A specimen of dihydroanhydroberberine which had crystallised from acetone in small crystals and melted at 167—168° was analysed in December, 1917, and yielded C=71·2, H=5·7, whereas $C_{20}H_{19}O_4N$ requires C=71·2, H=5·6 per cent. This specimen was left on a watch-glass in a large drawer which was in frequent use, fully exposed until the end of June, 1918, when it had not altered in appearance, still melted at 167—168°, and yielded on analysis C=71·1, H=5·6. In the second case, dihydroanhydroberberine hydrochloride, prepared from the pure base, was repeatedly recrystallised from dilute hydrochloric acid, and a portion taken and dried at 90°, when it yielded C=61·5, H=5·7, whereas $C_{20}H_{19}O_4N,HCl,H_2O$ requires C=61·3, H=5·6 per cent. The remainder (14 grams) was left on a porous plate exposed to the air, in the drawer already mentioned, for a like period of about six months, and had then the same brilliant appearance as at first. When a weighed portion was heated at 90° until constant, it lost 12·1 per cent., and the residue gave on analysis C=61·6, H=5·7, or almost exactly the same result as before exposure. It may be pointed out that these and other analytical results point to the formula $C_{20}H_{19}O_4N,HCl,4H_2O$ as representing the composition of dihydroanhydroberberine hydrochloride, and show that of the $4H_2O$, one remains at 90°, exactly as in the case of berberinium chloride, for $C_{20}H_{19}O_4N,HCl,4H_2O$, losing $3H_2O$, means a loss of 12·1 per cent., and the formula $C_{20}H_{19}O_4N,HCl,H_2O$ requires C=61·3, H=5·6 per cent. Gadamer states that his analytical results point to the formula $C_{20}H_{19}O_4N,HCl,3H_2O$, but

his determinations of water of crystallisation and chlorine* agree fairly well with the formula containing $4H_2O$.

Since there is little difference in composition between berberinium chloride, $C_{20}H_{18}O_4NCl$, and dihydroanhydroberberine hydrochloride, it was still necessary to prove that the salt which had been exposed to the air consisted of the latter substance. For this purpose, the hydrochloride (13·5 grams), dissolved in a little hot water, in which it is readily soluble, was made alkaline with ammonia and allowed to remain until the viscid precipitate had hardened. While still warm, the precipitate was collected, triturated with water, and thoroughly washed; it was then dried on porous porcelain in the steam-oven, and weighed 9·75 grams, whereas the amount of dihydroanhydroberberine which should have been produced from 13·5 grams of the pure hydrochloride, $C_{20}H_{19}O_4N,HCl,4H_2O$, is 10·2 grams. The base on crystallisation from methyl alcohol melted at 166—168°, and was pure dihydroanhydroberberine. The ammoniacal mother liquors gave, on concentration under diminished pressure and admixture with a large excess of hydrochloric acid, a slight crystalline precipitate. On remaining in the ice-chest, this increased somewhat, and, after collecting, washing with dilute hydrochloric acid, and drying in the steam-oven, it weighed 0·55 gram, and consisted of berberinium chloride. Apparently, therefore, oxidation had taken place, but to a very slight degree.

Crystallographical Examination and Comparison of Dihydroanhydroberberine and Tetrahydroanhydroberberine.

It has already been pointed out (p. 725) that Faltis (*Monatsh.*, 1910, **31**, 565) had expressed the opinion that the base obtained by the action of concentrated alkalis on the berberinium salts is not dihydroanhydroberberine, as claimed by Gadamer (*Arch. Pharm.*, 1905, **243**, 35), but is, in fact, tetrahydroanhydroberberine. In order the more effectually to disprove this view, specially pure preparations of the substances in question were made, crystallised from acetone, and several well-developed crystals of each carefully measured.† The author is indebted to Miss Porter and Mr. T. V. Barker for undertaking the measurements.

* There is a slip in the calculation of the chlorine content of

$$C_{20}H_{19}O_4N,HCl,3H_2O,$$

which should be 8·3 and not 9·5 per cent.

† Tetrahydroanhydroberberine, prepared by the reduction of berberinium chloride or sulphate with zinc and dilute acid, is rarely obtained colourless, and the crystals retain their colour persistently even after repeated recrystallisation. In order to remove the colour, a good plan is to recrystallise

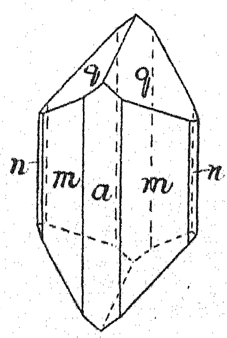
Dihydroanhydroberberine (M. W. Porter).

The crystals are monoclinic with the axial ratios: $a:b:c=1{\cdot}708:1:0{\cdot}831$; $\beta = 96°40'$. Determinants: $01\bar{1}/0\bar{1}\bar{1}/100$. Complex-symbol: $4h$;-$6\frac{1}{2}/59\frac{1}{2}/$-5. Forms observed: $a\{100\}$, $m\{110\}$, $n\{120\}$, $q\{011\}$. The crystals of this compound are slender, prismatic in habit, as shown in Fig. 1. The form $a\{100\}$ is fairly well developed, but $m\{110\}$ predominates. The faces of the form $n\{120\}$ are narrow. Four fairly good crystals were measured. The results of the measurements are shown below.

		Azimuth (ϕ).		
Face.	No. of readings.	Limits.	Obs.	Calc.
a (100)	7	89°47'—90°12'	89°59'	90°0'
m (110)	10	30 18 —30 40	*30 31	—
n (120)	9	16 30 —17 12	16 48	16 25
q (011)	6	7 35 — 8 14	*8 0	—

		Polar distance (ρ).		
Face.	No. of readings.	Limits.	Obs.	Calc.
a (100)	7	90°0' —90°8'	90°1'	90°0'
m (110)	10	90 0 —90 0	90 0	90 0
n (120)	9	90 0 —90 0	90 0	90 0
q (011)	6	39 51 —40 6	*40 0	—

FIG. 1.



Tetrahydroanhydroberberine (M. W. Porter).

The crystals are monoclinic and exhibit the forms $o\{111\}$, $o'\{\bar{1}11\}$, $a\{100\}$, and $c\{001\}$, with the octahedral habit shown in Fig. 2. Crystallographic constants: 47°54', a(48°17')m(41°43')b, 50°36', 89°4'; or, alternatively, $a:b:c=1{\cdot}121:1:0{\cdot}904$, $\beta=90°56'$.

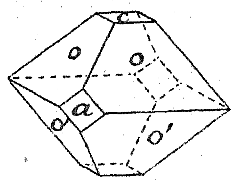
the hydrochloride from glacial acetic acid, in which it is rather sparingly soluble, until the salt is perfectly white and then to liberate the base and crystallise it from alcohol or acetone. Tetrahydroanhydroberberine purified in this way is perfectly colourless and melts at 174°.

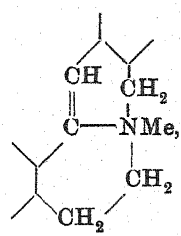
Determinants: 010/001/100. Complex-symbol: $4d$; $+1/59/+3$. Following are the mean observations from three crystals:

	a (100).	c (001).	o' ($\bar{1}$11).	o (111).	
Azimuth (ϕ)	Face of	90°0′	47°54′	*47°54′	
Polar distance (ρ) ...	reference	*89 4	*120 20½	58 38	(Calc. 58 37)

Although the crystals are pseudo-orthorhombic, an optical examination agreed with monoclinic symmetry.

FIG. 2.



Dihydroanhydroberberine Methosulphate, 

.

This substance may be prepared by adding excess of freshly distilled methyl sulphate (10 c.c.) to a solution of dihydroanhydroberberine (10 grams) in boiling benzene, when there is no immediate precipitate, but gradually the yellow methosulphate separates in prisms. After remaining overnight, the mass is collected, washed with benzene, and dried in the steam-oven, when a yield of 10 grams is obtained, and a further crop of less pure material separates from the concentrated mother liquor. The whole is crystallised from methyl alcohol, in which the methosulphate is sparingly soluble and from which it separates in well-developed prisms. A better method of preparation is to shake the base (10 grams) with methyl sulphate (15 c.c.) in a stoppered bottle, when a thin paste is formed without development of heat. On keeping, the paste gradually becomes thicker, and after eight days combination is complete. The product is triturated with benzene, filtered, and the residue crystallised from methyl alcohol. The comparative slowness of the combination is evidenced by the fact that, if the mass after two days is washed with benzene and boiled with water, only about half dissolves as the methosulphate, and the rest is unchanged dihydro-

anhydroberberine. For analysis, the air-dried substance was dried in the steam-oven, when it lost about 8 per cent.:

0·1168 gave 0·2435 CO_2 and 0·0578 H_2O. C = 56·8; H = 5·5.

$C_{20}H_{19}O_4N,Me_2SO_4$ requires C = 57·0; H = 5·4 per cent.

Dihydroanhydroberberine methosulphate shrinks at 140° and melts at about 205° to an amber syrup; it dissolves sparingly in cold, but readily in hot water, and separates as a very voluminous mass of microscopic, lemon-yellow needles which filter with difficulty. The air-dried crystals seem to contain $4H_2O$, since a specimen which had been exposed to the air for ten days gave the following results:

0·1132 lost 0·0147 at 100°. H_2O = 13·0.

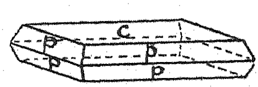
$C_{20}H_{19}O_4N,Me_2SO_4,4H_2O$ contains H_2O = 13·3 per cent.

The residue, 0·0985 gave 0·2050 CO_2 and 0·0485 H_2O. C = 56·8; H = 5·5 per cent.

Miss M. W. Porter was kind enough to examine some crystals of dihydroanhydroberberine methosulphate which had been obtained from methyl alcohol, and reports as follows:

The crystals are orthorhombic and exhibit the forms $c\{001\}$ and $p\{111\}$. The habit is tabular, parallel to c (see Fig. 3), which is a plane of perfect cleavage. The mean results of measurement for $p(111)$ are: azimuth $(\phi) = 48°40'$; polar distance $(\rho) = 64°26'$. Axial ratios: $a:b:c = 0·879:1:1·380$. Determinants: 010/100/001. Complex-symbol: $4d/64°26'/+3°40'$.

FIG. 3.



The aqueous solution of the methosulphate gives no precipitate on the addition of ammonia, even on boiling, but hot concentrated sodium hydroxide produces a milky solution from which a white, crystalline precipitate separates. The methosulphate is readily soluble in glacial acetic acid, and the addition of sulphuric acid produces a pink coloration which, on keeping, becomes more intense; a drop of dilute nitric acid changes this to deep claret and then to brown. The benzene washings of the crude methosulphate, as well as the aqueous and methyl-alcoholic mother liquors, contain a second substance, which is much more readily soluble than the methosulphate and can be separated from it by fractional crystallisation from water. The amber prisms obtained in this way, on the addition of ammonia to their aqueous solution,

gave a precipitate of dihydroanhydroberberine, and consist, therefore, evidently of *dihydroanhydroberberine methyl hydrogen sulphate*:

0·1002 gave 0·2055 CO_2 and 0·0475 H_2O. C=56·0; H=5·2.

$C_{20}H_{19}O_4N,MeHSO_4$ requires C=56·1; H=5·1 per cent.

When any considerable quantity of the crude mixture of methosulphate and methyl hydrogen sulphate accumulates, a good plan is to dissolve the whole in boiling water and add ammonia. The dihydroanhydroberberine which separates is rapidly collected, and is remarkably pure, whilst the hot filtrate, on keeping, deposits the pure methosulphate.

Dihydroanhydroberberine Methiodide, $C_{20}H_{19}O_4N,MeI$.—A boiling dilute solution of dihydroanhydroberberine methosulphate gives, on the addition of boiling dilute potassium iodide, a clear solution, from which the iodide immediately begins to crystallise as a lemon-yellow powder:

0·1175 gave 0·2265 CO_2 and 0·0472 H_2O. C=52·6; H=4·5.

$C_{21}H_{22}O_4NI$ requires C=52·6; H=4·5 per cent.

This iodide darkens rapidly above 190°, is brick-red at about 200°, and melts at about 215—220° with effervescence to a reddish-brown froth. It is very sparingly soluble in water, but comparatively readily so in boiling alcohol, from which it separates in thin, microscopic plates. This methiodide is evidently identical with the substance which Freund and Fleischer (*Annalen*, 1915, **409**, 231) obtained from dihydroanhydroberberine by the direct action of methyl iodide, which they found to melt at 223—224°.

The *methochloride*, $C_{20}H_{19}O_4N,MeCl$, was obtained by grinding the iodide to a paste with water, adding much water and freshly precipitated silver chloride, and heating on the water-bath for an hour. After filtering, the almost colourless solution was concentrated and allowed to remain, when a crust of glistening, well-developed, four-sided prisms separated, which were collected, ground, and allowed to remain exposed to the air for a week. The substance appears to contain $5H_2O$, of which $4H_2O$ are removed by drying at about 95°:

0·1287 lost 0·0229 at 95°. H_2O=17·7.

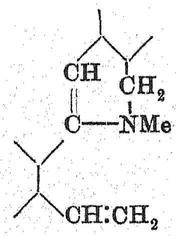
$C_{21}H_{22}O_4NCl,5H_2O$ losing $4H_2O$ requires H_2O=18·1.

After drying at 90°, 0·1267 gave 0·2890 CO_2 and 0·0671 H_2O. C=61·8; H=5·9.

$C_{21}H_{22}O_4NCl,H_2O$ requires C=62·1; H=5·9 per cent.

Dihydroanhydroberberine methochloride melts and decomposes at about 223° with evolution of gas to a brown syrup. It is sparingly soluble in cold, but readily so in boiling water, and a drop of the

solution mixed with dilute sulphuric acid gives, on the addition of a trace of manganese dioxide, a pink coloration which, on boiling, becomes claret coloured. It dissolves readily in hot glacial acetic acid and crystallises, on cooling, in needles. The addition of sulphuric acid to the solution of a crystal in a drop of glacial acetic acid produces an intense purple coloration. When the methochloride is heated in a drawn-out test-tube by means of a sulphuric-acid bath at 230° for a couple of minutes, methyl chloride is eliminated, and the solution of the dark brown residue in boiling methyl alcohol deposits pale brown crystals which melt at about 165—167°, and consist of dihydroanhydroberberine (compare this vol., p. 506).

Anhydromethylberberine,  .

Anhydromethylberberine is obtained when dihydroanhydroberberine methosulphate is digested with methyl-alcoholic potassium hydroxide, and it is important that the methosulphate should be quite free from dihydroanhydroberberine methyl hydrogen sulphate, otherwise the anhydromethylberberine will be contaminated with dihydroanhydroberberine, and then very difficult to purify. The methosulphate should therefore be recrystallised from methyl alcohol until its aqueous solution, on the addition of ammonia, remains perfectly clear, even on warming. The methosulphate (5 grams), dissolved in the least possible quantity of boiling methyl alcohol, is mixed with methyl-alcoholic potassium hydroxide (30 c.c. of 25 per cent.) and vigorously boiled, so that much of the methyl alcohol escapes. The clear solution soon clouds, and oily drops separate which sink to a yellow globule at the bottom of the vessel. After ten minutes, the whole is vigorously shaken under cold water in order to granulate the mass, water is added, the rather viscid precipitate collected, washed with water, and ground and washed with methyl alcohol, which removes a good deal of oily impurity and leaves a pale yellow, crystalline mass. Finally, the substance is rapidly crystallised from methyl alcohol or acetone. Difficulty was experienced in obtaining good analytical results until a lead chromate tube was employed:

0·1001 gave 0·2625 CO_2 and 0·0548 H_2O. C=71·5; H=6·1.
0·1012 „ 0·2664 CO_2 „ 0·0551 H_2O. C=71·8; H=6·1.
$C_{21}H_{21}O_4N$ requires C=71·8; H=6·0 per cent.

Anhydromethylberberine melts at 94—95°, and, like anhydrocryptopine (m. p. 110—111°, p. 975), is sparingly soluble in methyl alcohol, from which it crystallises, if the operation is carried out rapidly and with small quantities (see below), in fern-like groups of needles; it separates from acetone, in which it is readily soluble, in pale yellow prisms. Unfortunately, these are striated, and therefore unsuitable for measurement and comparison with the crystals of anhydrocryptopine (976).

Anhydromethylberberine is a weak base, since its bright yellow solution in glacial acetic acid is precipitated by water, and it does not dissolve in very dilute hydrochloric acid in the cold.

A trace of the substance dissolved in a drop of acetic acid gives with sulphuric acid a faint yellowish-brown solution which rapidly becomes chartreuse-green, and the addition of a trace of dilute nitric acid changes the colour to bright cherry-red.

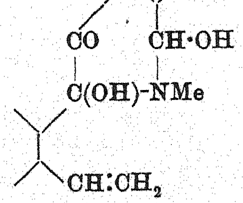
If benzenediazonium chloride is added to the solution in acetic acid, a deep orange-red coloration is produced, and precisely the same reaction is shown by anhydrocryptopine.

When boiled with methyl alcohol in contact with the air, anhydromethylberberine rapidly undergoes some profound change, since, although it is very sparingly soluble in this solvent in the cold, only a comparatively small part separates on keeping, particularly if the experiment has been carried out with large quantities of material and there is no further separation on concentrating the dark brown mother liquor. When the mother liquors from a number of crystallisations were allowed to remain in a flask exposed to the air, a crystalline crust gradually separated, and in some cases—notably when pure anhydromethylberberine had been recrystallised—the new substance separated in rosettes of garnet prisms, but the amount was always very small (990):

0·1039 gave 0·2393 CO_2 and 0·0511 H_2O. C=62·8; H=5·4.

$C_{21}H_{21}O_7N$ requires C=63·1; H=5·3 per cent.

This substance, which apparently contains the grouping



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and for which the name *trioxyanhydromethylberberine* is suggested, melts at 153—155° and is a very feeble base, since it does not dis-

solve in cold dilute hydrochloric acid; on boiling, decomposition appears to occur and a milky liquid is produced. The solution in glacial acetic acid is almost colourless, but becomes deep orange when mixed with sulphuric acid, and the addition of a trace of dilute nitric acid produces a dark brown coloration. The dark brown methyl-alcoholic mother liquors from which this substance had separated contained a large amount of a resinous substance, the nature of which has not been investigated.

Reduction of Anhydromethylberberine to N-*Methyl*iso*tetrahydroanhydroberberine* (*B*).—This reduction was carried out under the following conditions: Anhydromethylberberine, dissolved in warm concentrated hydrochloric acid or dilute sulphuric acid (20 per cent.), was immediately mixed with ice in a flat basin standing on powdered ice; a large excess of 4 per cent. sodium amalgam was then added, care being taken to keep the liquid strongly acid throughout the operation. If hydrochloric acid has been employed, the sparingly soluble hydrochloride of *N*-methyl*iso*tetrahydroanhydroberberine will have separated, and this is collected and recrystallised from much water or, better, dilute acetic acid.

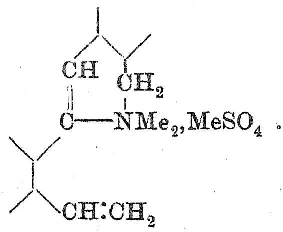
In the case of the use of sulphuric acid, which seems to lead to a rather better yield, the base is precipitated with ammonia, dissolved in dilute hydrochloric acid, and the hydrochloride recrystallised.

The pure hydrochloride is then decomposed and the base several times crystallised from methyl alcohol. (Found: C=71·1; H=6·5. $C_{21}H_{23}O_4N$ requires C=71·4; H=6·6 per cent.)

This substance melts at 113—115°, and was shown, by direct comparison, to be identical with *N*-methyl*iso*tetrahydroanhydroberberine (*B*), which Pyman (T., 1913, **103**, 827, 835) obtained by the dehydration of tetrahydroanhydroberberine methohydroxide. The *hydriodide*, $C_{21}H_{23}O_4N,HI$, which does not appear to have been described, was prepared by adding boiling dilute potassium iodide to the boiling solution of the hydrochloride, when there was no immediate precipitate, but, on keeping, the hydriodide separated in rather indefinite balls of needles. It darkens at 220° and melts rather sharply at 225° with decomposition:

0·1005 gave 0·1938 CO_2 and 0·0461 H_2O. C=52·6; H=4·5.

$C_{21}H_{24}O_4NI$ requires C=52·4; H=4·9 per cent.

Anhydromethylberberine Methosulphate, 

In preparing this substance, anhydromethylberberine (15 grams) was mixed with methyl sulphate (20 c.c.) in a bottle and well shaken, when the feebly basic nature of the substance was evidenced by the fact that there was no rise of temperature and no apparent immediate action. During twenty-four hours much had dissolved, and gradually the whole became a viscid syrup which, on further shaking, set to a semi-solid mass. After seven days, the mass was triturated with benzene, collected, washed with benzene, and left exposed until free from the solvent. It was then dissolved in boiling water, from which it separated readily in leaflets, and once it is recrystallised it becomes sparingly soluble in water. On keeping exposed to the air, the crystals lose their lustre, but the air-dry substance does not lose weight in the steam-oven, although it still appears to contain $1H_2O$:

0·1218 gave 0·2508 CO_2 and 0·0652 H_2O. C = 56·1; H = 5·9.

$C_{21}H_{21}O_4N,Me_2SO_4,H_2O$ requires C = 55·8; H = 5·7 per cent.

Anhydromethylberberine methosulphate melts at about 150—152° with vigorous effervescence, due to the escape of steam, and the brown syrup, which remains, dissolves in hot water and separates on cooling in white leaflets. It crystallises from water in colourless, flat needles, and is readily soluble in boiling methyl alcohol, from which it separates in groups of thin plates. A trace of the substance dissolved in a drop of glacial acetic acid gives, with sulphuric acid, a pink solution, and a drop of dilute nitric acid added to this changes the colour first to intense blue and then to brown.

When the solution in boiling methyl alcohol is mixed with methyl-alcoholic potassium hydroxide and heated on the steam-bath, it soon becomes milky, and an oil separates after a few minutes. The product was mixed with water, the viscid precipitate collected, washed, and dissolved in boiling methyl alcohol, from which, on rubbing with a glass rod, minute yellow prisms separated which melted at 92—94°, and consisted of anhydromethylberberine (979).

Anhydromethylberberine Methiodide, $C_{21}H_{21}O_4N,MeI$.—When

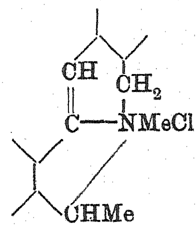
boiling dilute potassium iodide is added to the boiling dilute solution of the methosulphate, a clear solution is obtained, and remains for some time, but, on rubbing with a glass rod, the iodide immediately commences to separate in groups of flat prisms:

0·1040 gave 0·2052 CO_2 and 0·0461 H_2O. C=53·7; H=4·9.

$C_{22}H_{24}O_4NI$ requires C=53·5; H=4·9 per cent.

This methiodide becomes brown at 185° and melts at 188—190° with vigorous decomposition to a brown froth (980). It is comparatively readily soluble in boiling water, but sparingly so in the cold, and the hot solution, on cooling, becomes milky and then crystallises. It is rather readily soluble in boiling alcohol and separates in groups of striated plates.

ψ-Methylberberinium Chloride,



This interesting substance is obtained from anhydromethylberberine methosulphate by the action of concentrated hydrochloric acid (984).

The methosulphate (1 gram), dissolved in concentrated hydrochloric acid (3 c.c.), is heated to boiling for five minutes in a sulphuric acid bath and the hydrochloric acid distilled off under diminished pressure. When the pale brown residue is dissolved in a small quantity of boiling water and stirred, crystallisation soon sets in, and the chloride separates in striated, hexagonal plates.

The ochreous mass is collected, dissolved in a little boiling water, and mixed with an equal volume of concentrated hydrochloric acid, when the chloride separates in characteristic balls of needles or plates, according to the concentration. The substance contains water of crystallisation, which was not determined, and, after drying at 70° and then over phosphoric oxide in a vacuum desiccator, the following analyses indicate that it still contains $1H_2O$:

0·1112 gave 0·2568 CO_2 and 0·0590 H_2O. C=63·0; H=5·9.
0·1118 ,, 0·2562 CO_2 ,, 0·0597 H_2O. C=62·5; H=5·9.

$C_{21}H_{22}O_4NCl,H_2O$ requires C=62·1; H=5·9 per cent.

ψ-Methylberberinium chloride softens at 80—82°, gradually shrinks, and becomes a syrup below 100°. It is readily soluble in warm water or methyl alcohol, but insoluble in ether, and when

ether is added to the solution in methyl alcohol, a milky liquid results, from which the chloride rapidly separates in highly characteristic stars of pale yellow needles. The solution of a trace of the chloride in a drop of acetic acid gives, on the addition of sulphuric acid, at first no coloration, but a salmon tint soon develops and rapidly changes to intense permanganate colour. A splinter of the chloride on a watch-glass, when moistened with concentrated nitric acid, dissolves to an intense crimson solution. The aqueous solution of the chloride is coloured yellow by ammonia, but gives no precipitate, and it behaves in the same way with cold sodium hydroxide, but when placed in the steam-bath the yellow solution becomes orange, then brown, and a dirty green base separates. The addition of methyl-alcoholic potassium hydroxide to the methyl-alcoholic solution of the chloride causes a separation of potassium chloride, but the yellowish-brown solution yields no precipitate with water. If the solution in dilute methyl-alcoholic potassium hydroxide is heated in the steam-bath, the liquid on the side of the test-tube dries to a brilliant crimson; after a time, this no longer occurs, and a black, amorphous precipitate separates which dissolves in hydrochloric acid to a brownish-pink solution. Even when mixed with powdered ice, the aqueous solution of the chloride instantly decolorises permanganate (984).

The *platinichloride*, $(C_{21}H_{22}O_4N)_2PtCl_6$, is a pale salmon coloured precipitate, and it is curious that when it is filtered off, the mother liquor is deep pink, exactly as was observed in the case of the preparation of the platinichloride from ψ-cryptopine chloride (985). When heated in a capillary tube, it loses its salmon colour at 200° and becomes yellow, then gradually darkens, shrinks together above 210°, and melts at about 243° with effervescence to a black tar:

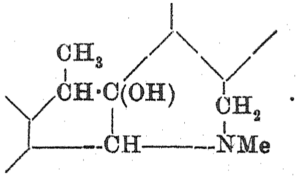
0·1216 gave 0·2026 CO_2 and 0·0435 H_2O. C=45·4; H=4·0.
0·2124 ,, 0·0366 Pt. Pt=17·2.
$(C_{21}H_{22}O_4N)_2PtCl_6$ requires C=45·3; H=4·0; Pt=17·5 per cent.

ψ-Berberinium Iodide, $C_{21}H_{22}O_4NI$.—The hot dilute solution of the chloride gives, with potassium iodide, a clear solution which may not crystallise for days, but gradually deposits groups of almost colourless warts:

0·1072 gave 0·2068 CO_2 and 0·0471 H_2O. C=52·6; H=4·8.
$C_{21}H_{22}O_4NI$ requires C=52·6; H=4·6 per cent.

This iodide darkens at 160—165° and decomposes at 175—180° to a brown mass. It is very sparingly soluble in water, more readily so in boiling alcohol, from which it separates in microscopic groups of needles.

The Hydroxyisoanhydrodihydromethylberberines, (A) and (B).



These substances, which correspond with the hydroxy*iso*anhydrodihydrocryptopines, (*A*) and (*B*), result from the action of dilute hydrochloric acid on anhydromethylberberine. The base (2 grams) is mixed with concentrated hydrochloric acid (2·5 c.c.) and water (8 c.c.) in a test-tube, when the crystals, although they appear to change, do not dissolve, but pass rapidly into solution on warming with the formation of a yellow liquid. The test-tube is placed in boiling water, which causes the colour to deepen considerably, and after twenty minutes the tube is withdrawn, when, in a short time, the liquid clouds and a heavy syrup separates which, on keeping, becomes a hard button.

The product may be worked up in two different ways.

(i) The whole is dissolved in hot water, made strongly alkaline with ammonia, and the chalky precipitate immediately extracted with much ether, in which, in this condition, it is readily soluble. The ethereal solution is washed, rapidly dried over anhydrous potassium carbonate, and concentrated, during which, and while the solution is still boiling, a crystalline crust of prisms begins to separate, and increases very much on keeping.* If the ethereal solution is not too concentrated, this substance, after collecting and washing with ether, may melt at once at 208—210°, and consist of almost pure hydroxy*iso*anhydrodihydromethylberberine (*A*). If this is not the case, the substance is recrystallised from ether or from methyl alcohol.

The modification (*B*) of the hydroxy-compound is contained in

* In the description of hydroxy*iso*anhydrodihydrocryptopine (*A*) (996), it is stated that attempts to obtain this base in a crystalline condition were unsuccessful. This may, however, be accomplished by employing ether as the solvent. The hydrochloride (m. p. 227°) is dissolved in hot water, the solution cooled, and covered with much pure ether; on the addition of excess of ammonia and shaking, the base passes readily into solution. The ethereal solution is dried over potassium carbonate and concentrated, when, on remaining in a closed flask for some months in the ice-chest, nodular masses separate which melt at 177–180°. (Found, C=68·0; H=6·3. $C_{21}H_{23}O_5N$ requires C=68·3; H—6·2 per cent.) The nodules dissolve readily in boiling methyl alcohol or acetone and separate, on long keeping, in microscopic prisms.

the ethereal mother liquors, and is isolated in the manner described below.

(ii) A method of separation which allows of the modification (*A*) being rapidly obtained in a pure condition depends on the fact that this modification is much less readily soluble in cold methyl alcohol than the modification (*B*). The chalky precipitate, obtained as just described, is dried on porous porcelain, triturated with methyl alcohol, filtered, and the residue washed with methyl alcohol two or three times. After drying, the almost colourless mass melts at about 195—197°, and one recrystallisation from methyl alcohol is sufficient to raise the melting point to 210—212°, and the substance is then the pure modification (*A*). The methyl-alcoholic mother liquors are then mixed with water, the base extracted with ether, and the ethereal solution washed well, dried over potassium carbonate, and fractionally concentrated, when crops of crystals of varying composition are obtained, and these are comparatively easily separated into the pure modifications (*A*) and (*B*) by recrystallisation from methyl alcohol or ether.

*Hydroxy*iso*anhydrodihydromethylberberine* (*A*) is very sparingly soluble even in boiling methyl alcohol, separates in rather indefinite crusts, and melts at 210—212°. It is also sparingly soluble in boiling benzene, acetone, light petroleum, or ether, but dissolves somewhat in boiling methylal, and separates, on cooling, in warty groups:

0·1021 gave 0·2546 CO_2 and 0·0566 H_2O. C=68·0; H=6·2.
0·1135 ,, 3·8 c.c. N_2 at 16° and 755 mm. N=3·8.
$C_{21}H_{23}O_5N$ requires C=68·3; H=6·2; N=3·8 per cent.

The base dissolves readily in dilute mineral acids, and as the solutions remain without crystallising, often for days, it was at first thought that the salts were very readily soluble. This is, however, not so, because in the case of the hydrochloride, for example, if a crystal of the hydrochloride (see below) is introduced into the warm, clear solution of the salt, a very sparingly soluble salt separates as a sandy, rather indefinitely crystalline powder. The characteristic behaviour of this base towards acids is well shown by rubbing a few crystals with dilute hydrochloric acid in a test-tube, when most dissolves, but some adheres to the sides as a gum. If the test-tube is placed in hot water, the gum immediately begins to crystallise, and, on stirring, the solution becomes filled with the hydrochloride, which is now remarkably sparingly soluble in boiling dilute hydrochloric acid. The base is readily soluble in acetic acid, and the addition of sulphuric acid produces a deep orange coloration.

*Hydroxy*iso*anhydrodihydromethylberberine* (*B*) separates from ethereal solution, on spontaneous concentration, in single, glistening prisms, very different in appearance from the hard crusts of the modification (*A*). It melts at 168—170°, and is generally more readily soluble than the modification (*A*). It is rather sparingly soluble in cold methyl alcohol, but readily so on warming, and separates on slow cooling in glistening prisms:

0·1032 gave 0·2589 CO_2 and 0·0580 H_2O. C=68·4; H=6·2.

$C_{21}H_{23}O_5N$ requires C=68·3; H=6·2 per cent.

This base does not show the behaviour with hydrochloric acid so characteristic of the modification (*A*). It is readily soluble in warm dilute hydrochloric acid, and, on cooling, the solution clouds and deposits a yellow syrup which gradually hardens, but shows little tendency to crystallise.

*Action of Acetyl Chloride on the Hydroxy*iso*anhydrodihydromethylberberines, (A) and (B).*

The modifications (*A*) and (*B*) of this hydroxy-derivative both yield the same products when they are subjected to the action of acetyl chloride at 100°. In each case, the base (1 gram) was sealed up with freshly distilled acetyl chloride (2 c.c.), when action took place at once with some evolution of heat, and a lemon-yellow, sandy precipitate separated. After the tube had been heated in boiling water for fifteen minutes, the excess of acetyl chloride was evaporated and the residue mixed with much cold water, which caused it to become pale green. On heating to boiling, the green colour disappeared, and a viscid precipitate (*C*) separated, which was collected and washed with warm water. This hydrochloride dissolves in boiling methyl alcohol, and, on cooling, rhombic plates gradually separate of angle 78° which are strongly doubly refracting and show straight extinction:

0·1073 gave 0·2415 CO_2 and 0·0562 H_2O. C=61·4; H=5·8.

$C_{23}H_{25}O_6N,HCl$ requires C=61·6; H=5·8 per cent.

This hydrochloride melts at about 253° with vigorous decomposition to a reddish-brown froth. It dissolves in much boiling water, but is remarkably sparingly soluble in boiling dilute hydrochloric acid, and separates in groups of thin laminæ with arrow-shaped ends. The hot aqueous solution yields, on the addition of ammonia, a milky liquid which soon begins to deposit colourless, crystalline flakes, and after these had been collected and washed and left to dry on porous porcelain, they were found to melt in the steam-oven and to solidify, on cooling, to a colourless resin. In contact with methyl alcohol, this resin at once became crystal-

line, dissolved on boiling, and well-developed, flat prisms separated, on keeping, which melted sharply at 166—167°:

0·1059 gave 0·2611 CO_2 and 0·0595 H_2O. C=67·1; H=6·2.

$C_{23}H_{25}O_6N$ requires C=67·2; H=6·1 per cent.

The methyl-alcoholic mother liquors, when left exposed to the air, deposited warty masses which melted at 208—210°, and consisted of hydroxy*iso*anhydrodihydromethylberberine (*A*), and it would therefore seem that the substance melting at 165—167° is the acetyl derivative of this modification (*A*). This is confirmed by the fact that this acetyl base yields, on treatment with hydrochloric acid, a very sparingly soluble hydrochloride which separates from methyl alcohol in rhombs with the angle 78°, and melts and decomposes at 253°.

The mother liquors and washings of the hydrochloride (*C*, see above) gave with ammonia a chalky precipitate, which was collected and crystallised from methyl alcohol, in which it was sparingly soluble, and from which it separated in crusts of nodules melting at 213—215° (*D*):

0·1061 gave 0·2638 CO_2 and 0·0593 H_2O. C=67·8; H=6·2.

$C_{23}H_{25}O_6N$ requires C=67·2; H=6·1 per cent.

This substance is presumably the acetyl derivative of hydroxy*iso*anhydrodihydromethylberberine (*B*). When it was mixed with warm dilute hydrochloric acid, it was converted into the hydrochloride, which separated from methyl alcohol in oblique, rhombic plates with an angle of 70°. After drying in the steam-oven until constant in weight, this salt yielded the following analysis:

0·1189 gave 0·2716 CO_2 and 0·0650 H_2O. C=62·3; H=6·0.

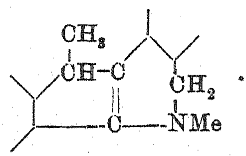
$C_{23}H_{25}O_6N,HCl$ requires C=61·6; H=5·8 per cent.

This hydrochloride darkens above 220° and decomposes at 230° with vigorous effervescence to an orange syrup. It dissolves readily in hot water and separates in a very characteristic manner, namely, in very thin, perfectly formed, nearly square plates with bevelled edges.

The mother liquors from this hydrochloride deposit, on concentration, rhombic prisms of angle 78°, which melt at 253—255° with vigorous effervescence, and evidently consist of the hydrochloride (*C*), partial molecular change having taken place during the conversion of the acetyl base (*D*) into the hydrochloride. That intramolecular changes of this nature take place readily under a variety of conditions is evidenced by the two following experiments, which were made with the object of determining whether it was possible to obtain base (*B*) from the acetyl derivative (*D*) by hydrolysis, and thus to confirm the relationship of these substances.

(i) The acetyl derivative (*D*) was boiled with dilute sulphuric acid (20 per cent.) for ten minutes, ammonia was then added, and the base crystallised from methyl alcohol, from which it separated as a rather indefinite, crystalline crust melting at 209—211°, and consisting of hydroxy*iso*anhydrodihydroberberine (*A*). The methyl-alcoholic mother liquors deposited, on slow evaporation in the ice-chest, groups of needles which melted at 165—168°, and proved to be the modification (*B*) of the same hydroxy-base.

(ii) The acetyl derivative (*D*) was boiled with 10 per cent. methyl-alcoholic potassium hydroxide until it had dissolved and the solution concentrated, when, on keeping in the ice-chest, a crystalline substance separated which melted at 208—210°, and consisted of modification (*A*) of the hydroxy-derivative.

iso*Anhydromethylberberine*, 

The hydrochloride of this base may be obtained from either of the hydroxy*iso*anhydrodihydromethylberberines, (*A*) or (*B*), by boiling with concentrated hydrochloric acid or, better, by digesting with phosphoryl chloride. The following two experiments will illustrate this conversion.

(i) Hydroxy*iso*anhydrodihydromethylberberine (*B*, 2 grams) was boiled with concentrated hydrochloric acid (20 c.c.) for half an hour by means of a sulphuric acid bath, during which a sparingly soluble hydrochloride separated as a crust on the sides of the test-tube. The hydrochloric acid was distilled off under diminished pressure, the pale ochreous residue dissolved in much boiling water, the solution concentrated, and left in the ice-chest, when a considerable crop of the hydrochloride of *iso*anhydromethylberberine gradually separated.

(ii) Hydroxy*iso*anhydrodihydromethylberberine (*A*, 2 grams) was mixed with freshly distilled phosphoryl chloride (6 c.c.), in which it did not dissolve in the cold, but, on warming, solution took place readily with the evolution of sufficient heat to raise the temperature from 60° to the boiling point. After boiling for ten minutes, the excess of oxychloride was distilled off under 15 mm. pressure, and the deep yellow gum dissolved in much boiling water, when, on concentration and vigorous stirring, a large crop of the sparingly soluble hydrochloride of *iso*anhydromethylberberine separated.

The hydrochloride from either (i) or (ii) was recrystallised from much hot water, dissolved in boiling water, and mixed with ammonia, when a milky liquid resulted which soon crystallised, and the base was further purified by crystallisation from methyl alcohol:

0·1011 gave 0·2655 CO_2 and 0·0545 H_2O. C=71·6; H=6·0.
$C_{21}H_{21}O_4N$ requires C=71·8; H=6·0 per cent.

iso*Anhydromethylberberine* melts at 123—124° and is readily soluble in methyl alcohol, separating in glistening prisms, which, however, were not suitable for measurement and comparison with the crystals of *iso*anhydrocryptopine (1003). It is very readily soluble in benzene, but rather sparingly so in light petroleum; it may, however, be crystallised from light petroleum (b. p. 80—90°), from which it separates in groups of needles like fern fronds. It is very readily soluble in ether, and crystallises well from this solvent. It dissolves readily in acetic acid, and the addition of sulphuric acid produces a deep orange colour, which becomes brown on adding a drop of dilute nitric acid. When the base is heated in a test-tube, there is much charring and the development of a strong odour of dimethylamine.

The Hydrochloride, $C_{21}H_{21}O_4N,HCl$.—This salt is sparingly soluble in water, and particularly so in dilute hydrochloric acid, and separates in brilliant, elongated prisms which are somewhat curved. It crystallises from methyl alcohol in brilliant, prismatic tablets with many facets, and melts at about 205—210° with previous softening.

The air-dried salt lost 3·7 per cent. at 100°, and gave the following results:

0·1066 gave 0·2538 CO_2 and 0·0556 H_2O. C=64·9; H=5·8.
$C_{21}H_{21}O_4N,HCl$ requires C=64·9; H=5·7 per cent.

The Hydriodide.—A boiling dilute aqueous solution of the hydrochloride gives no precipitate on adding boiling dilute potassium iodide, but, on keeping, the iodide soon commences to separate in indefinite, nodular groups:

0·1092 gave 0·2113 CO_2 and 0·0455 H_2O. C=52·7; H=4·6.
$C_{21}H_{21}O_4N,HI$ requires C=52·6; H=4·6 per cent.

When quickly heated, this hydriodide does not discolour until about 215°, and decomposes at about 247° to a nearly black froth. It is almost insoluble in cold water and sparingly so in cold alcohol, but it dissolves comparatively readily in boiling alcohol and separates in two distinct forms, namely, in stars or groups of needles or in short, brilliant prisms. When the solution is warmed,

the needles dissolve and leave the prisms, and it is evident, therefore, that this salt is dimorphic.

Action of Dilute Sulphuric Acid on iso*Anhydromethylberberine.*

The sulphate of *iso*anhydromethylberberine is readily soluble, and if the solution in a large excess of dilute sulphuric acid is boiled for half an hour and then made alkaline with ammonia, an amorphous base separates, which may be extracted with ether. The ethereal solution was thoroughly washed, dried over potassium carbonate, and concentrated, when, on remaining in the ice-chest for several days, a crust of needles formed, but in comparatively small amount. The substance was collected, washed with ether, in which it was sparingly soluble, and crystallised from methyl alcohol, in which the base is remarkably sparingly soluble, and from which it separated as a crystalline crust.

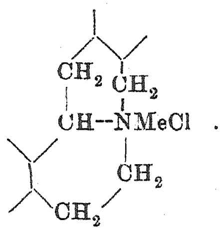
It melted at 212—215°, and consisted of hydroxy*iso*anhydrodihydromethylberberine (*A*). (Found: C = 68·4; H = 6·1. $C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2 per cent.) The ethereal mother liquor from the crystallisation of this modification yielded, on concentration, a small quantity of the modification (*B*) melting at 165—167° (compare p. 732).

Reduction of Dihydroanhydroberberine Methochloride.

In studying this reduction, the methochloride (30 grams), dissolved in hot water (1 litre), was mixed with concentrated hydrochloric acid (50 c.c.) and heated to boiling in an enamelled basin. Sodium amalgam (1500 grams of 3 per cent.) was then added, in three portions, together with sufficient hydrochloric acid to keep the liquid strongly acid. The product, separated from the mercury, clouded on cooling, and when mixed with excess of ammonia deposited a viscid, pale brown precipitate which, on keeping, soon hardened. This was collected, washed with a little warm water, dried on porous porcelain, and extracted with ether (*X*), which left a nearly colourless mass undissolved.

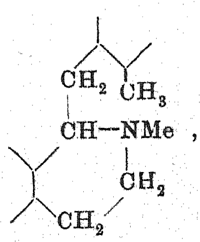
The latter was found to consist of a quaternary chloride, and a further considerable quantity of the same substance was obtained from the washings of the precipitate which had separated on the addition of ammonia. The whole was repeatedly crystallised from hot dilute hydrochloric acid, and thus separated into two quaternary chlorides, (α) and (β), melting approximately at 245—250° and 280—285° respectively. The chloride (α) is, after drying at 100°, anhydrous, and has the formula $C_{21}H_{24}O_4NCl$. (Found: C = 64·5; H = 6·3. Calc.: C = 64·7; H = 6·2 per cent.) The chloride (β),

melting at 280—285°, retains $1H_2O$ after drying at 100°. (Found: C=61·7; H=6·3. $C_{21}H_{24}O_4NCl,H_2O$ requires C=61·8; H=6·4 per cent.) There can be no doubt that these substances are the *α*- and *β*-methochlorides of tetrahydroanhydroberberine (compare p. 733),



first described by Pyman (T., 1913, **103**, 825, 826), and this was confirmed by the fact that the *β*-chloride, on digesting with methyl-alcoholic potassium hydroxide, yielded a base which separated from methyl alcohol in colourless nodules, melted at 108—110°, and consisted of methyl*iso*tetrahydroanhydroberberine (base *B*), which Pyman obtained by the dehydration of tetrahydroanhydroberberine methohydroxide (*loc. cit.*, p. 827). The identity was confirmed by analysis. (Found: C = 71·2; H = 6·6. $C_{21}H_{23}O_4N$ requires C=71·4; H=6·5 per cent.)

The ethereal extract (*X*) from the crude quaternary chlorides (see above) was thoroughly washed with water, dried over potassium carbonate, and evaporated, when a syrup was obtained which, even on long keeping in the ice-chest and frequent stirring, showed no signs of crystallising. That this substance is *dihydromethyl*iso-*tetrahydroanhydroberberine* (p. 733),



is indicated by its properties, and an analysis supported this view and suggested that the base was nearly pure:

0·1046 gave 0·2730 CO_2 and 0·0672 H_2O. C=71·3; H=7·1.

$C_{21}H_{25}O_4N$ requires C=71·0; H=7·0 per cent.

The salts are readily soluble and exhibit little tendency to crystallise. The *platinichloride* was prepared by adding platinic

chloride to a dilute solution of the hydrochloride, and is a chalky, salmon coloured precipitate:

0·1021 gave 0·1703 CO_2 and 0·0437 H_2O. C=45·5; H=4·7.
0·4764 ,, 0·0802 Pt. Pt=16·9.
$(C_{21}H_{25}O_4N)_2H_2PtCl_6$ requires C=45·0; H=4·7; Pt=17·4 per cent.

The Methosulphate.—This derivative was prepared by adding methyl sulphate (3 c.c.) to the solution of the base (3 grams) in warm benzene (15 c.c.), when a rise of temperature was observed, but there was no separation even after keeping for three days in the ice-chest.

On the addition of dry ether, the methosulphate was precipitated as a syrup, and was washed with ether, dissolved in a little methyl alcohol, and boiled with a considerable excess of methyl-alcoholic potassium hydroxide for fifteen minutes under such conditions that most of the methyl alcohol distilled away. Water was added, the caseous precipitate extracted with much ether, the ethereal solution thoroughly washed, dried over potassium carbonate, and evaporated, when a syrup remained which, on keeping, gradually crystallised to a striated mass of needles.

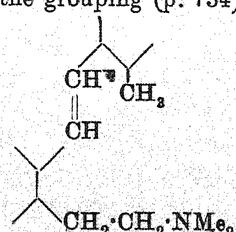
This was dissolved in dilute hydrochloric acid, the solution filtered, made alkaline with ammonia, and again extracted with ether, the ethereal solution being dried over potassium carbonate and evaporated, when the syrup again crystallised. After remaining in contact with porous porcelain over phosphoric oxide for several days, the following results were obtained on analysis:

0·1112 gave 0·2894 CO_2 and 0·0735 H_2O. C=71·0; H=7·3.
$C_{22}H_{27}O_4N$ requires C=71·5; H=7·3 per cent.

This base is very readily soluble in the usual solvents, and all attempts to recrystallise it were unsuccessful. The *platinichloride*, prepared in the usual manner, is a pale ochreous precipitate:

0·1017 gave 0·1731 CO_2 and 0·0449 H_2O. C=46·4; H=4·9.
0·4759 ,, 0·0798 Pt. Pt=17·0.
$(C_{22}H_{27}O_4N)_2H_2PtCl_6$ requires C=46·0; H=4·9; Pt=16·9 per cent.

The analytical results and the properties of this base leave little doubt that it is *dihydrodimethyl*iso*tetrahydroanhydroberberine* (950), and contains the grouping (p. 734)

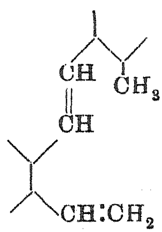


The *methosulphate* was prepared by dissolving the base (5 grams) in benzene and adding methyl sulphate (5 c.c.), when there was a considerable rise of temperature, and a syrup separated which soon commenced to crystallise and, on remaining in the ice-chest, became a soft mass of glistening needles. The crystals were collected, washed with benzene, transferred to porous porcelain, dried, and analysed:

0·1182 gave 0·2506 CO_2 and 0·0701 H_2O. C=57·8; H=6·6.

$C_{22}H_{27}O_4N,Me_2SO_4$ requires C=58·2; H=6·6 per cent.

This methosulphate is readily soluble in water or methyl alcohol and difficult to recrystallise, but it separates, when its solution in water is allowed to concentrate over sulphuric acid, as a soft mass of needles.

Berberidene,  .

In preparing this interesting substance, the methosulphate of dihydrodimethyl*iso*tetrahydroanhydroberberine was digested on the steam-bath with a large excess of methyl-alcoholic potassium hydroxide (20 per cent.), when decomposition readily set in with the elimination of trimethylamine. After twenty minutes, most of the methyl alcohol was distilled off, water was added, and the caseous precipitate extracted with much ether, in which in this condition it is moderately readily soluble. The ethereal solution was very thoroughly washed, dried over potassium carbonate, and concentrated, when, on keeping, the new substance separated as a crust of brilliant prisms:

0·1115 gave 0·3029 CO_2 and 0·0625 H_2O. C=74·1; H=6·2.

0·1062 ,, 0·2877 CO_2 ,, 0·0592 H_2O. C=73·9; H=6·2.

$C_{20}H_{20}O_4$ requires C=74·1; H=6·2 per cent.

Berberidene melts at 113—114°, and is characterised by the facility with which it crystallises. It is very sparingly soluble even in boiling methyl alcohol, and separates as a voluminous, glistening mass of irregular laminæ which, when free from any yellow mother liquor, have a most striking lilac fluorescence. It is readily soluble in benzene, but sparingly so in light petroleum, from which it separates in groups of needles. It is sparingly soluble in acetic acid in the cold, but dissolves readily on boiling,

and separates in rhombs or in brilliant, stout prisms with an oblique termination; if, however, the separation takes place rapidly, the crystallisation may be indefinite. Berberidene exhibits a very striking difference in its behaviour with methyl and ethyl alcohols. Whilst it is very sparingly soluble in methyl alcohol and crystallises well from this solvent, it dissolves quite readily in ethyl alcohol and separates only from quite concentrated solutions, and then as an indefinite crust composed of warts.

Oxidation of Berberidene.

In studying this oxidation (p. 735), finely sieved permanganate (4 grams) was gradually added, at the ordinary temperature, to the pure substance (2·3 grams) dissolved in acetone (60 c.c.), when oxidation took place readily with distinct rise of temperature, but care was taken that this did not exceed 18°. The product was filtered, the manganese precipitate thoroughly washed with acetone (*A*), and repeatedly extracted with small quantities of boiling water. The brown, aqueous extract was considerably concentrated and acidified with hydrochloric acid, when a viscid, brown acid separated which proved difficult to purify, but ultimately the following process was successful: The brown mass (about 1 gram) was boiled with water (200 c.c.) and filtered from the dark brown tar; the latter was warmed with dilute ammonia, when nearly all dissolved, and, after boiling with animal charcoal and filtering, the acid was again precipitated and boiled with water (100 c.c.). The combined aqueous extracts were neutralised with sodium carbonate, mixed with a little animal charcoal, evaporated to about 20 c.c., and filtered.

The nearly colourless filtrate gave, on acidifying, a chalky precipitate which melted at about 174°, and separated from glacial acetic acid as a satiny mass of plates. (Found: C=61·0; H=6·1. $C_{10}H_{12}O_4$ requires C=61·2; H=6·1 per cent.)

The pure acid melted at 183—184°, and was found by direct comparison to be identical with 5:6-*dimethoxy*-o-*toluic acid*, $C_6H_2Me(OMe)_2{\cdot}CO_2H$, which had been previously obtained (921) by the methylation of 5:6-dihydroxy-*o*-toluic acid. The melting point is there given as 177°, but repeated recrystallisation from glacial acetic acid raises this to 184°.

The mother liquors from the purification of the 5:6-dimethoxy-*o*-toluic acid were concentrated under diminished pressure until nearly dry, mixed with sand, and extracted with ether in a Soxhlet apparatus. The ethereal solution yielded, on evaporation, a small, crystalline residue which was separated by crystallisation from hydrochloric acid into 5:6-dimethoxy-*o*-toluic acid, and a more

readily soluble acid which separated from a little water in six-sided plates melting at about 171—174°, and, on heating, yielded an anhydride melting at about 170—173°. Since this acid gave a negative result for methoxy-groups in the Zeisel apparatus, there can be little doubt that it was hydrastic acid, $CH_2:O_2:C_6H_2(CO_2H)_2$, but the quantity was insufficient for analysis. The acetone extract (*A*) of the manganese precipitate yielded, on evaporation, a syrup (1·2 grams) which gradually crystallised in nodular masses. When this was submitted to distillation in a current of steam, a cloudy distillate was obtained in which oily drops were visible. The whole was extracted with pure ether, the ethereal solution washed, dried over potassium carbonate, and evaporated, when a colourless oil remained which rapidly crystallised in long needles. The crystals were left in contact with porous porcelain until quite dry, melted, and, after again crystallising, transferred once more to porous porcelain. Finally, the substance was dried over phosphoric oxide in a vacuum desiccator and analysed. (Found: C=66·5; H=6·8. $C_{10}H_{12}O_3$ requires C=66·7; H=6·7 per cent.)

This substance was 5:6-dimethoxy-*o*-tolualdehyde,

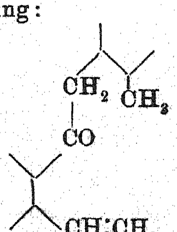
$$C_6H_2Me(OMe)_2 \cdot CHO,$$

since it melted at 52—53°, and, when mixed with a specimen of this aldehyde which had previously been obtained by the methylation of 5-methoxy-*o*-tolualdehyde (915), there was no alteration in melting point.

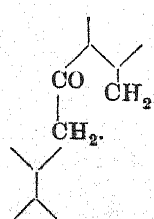
The residue in the steam distillation flask contained a viscid oil, which was extracted with ether, the ethereal solution washed well, dried over potassium carbonate, and evaporated, when a pale yellow syrup remained, which soon began to crystallise in nodules and ultimately became solid. The mass was triturated with methyl alcohol, which removed oily impurity, transferred to porous porcelain, and recrystallised from glacial acetic acid:

0·1265 gave 0·3285 CO_2 and 0·0679 H_2O. C=70·8; H=6·1.
$C_{20}H_{20}O_5$ requires C=70·6; H=5·9 per cent.

Since this substance yields a semicarbazone (see below), there can be little doubt that it is *ketodihydroberberidene* and contains the grouping:



or



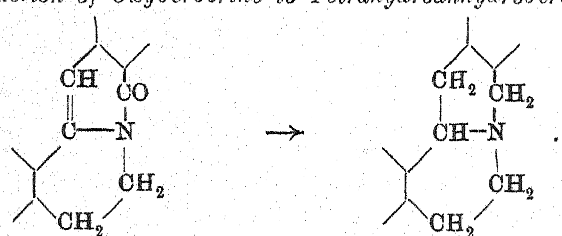
It is rather sparingly soluble in cold glacial acetic acid, much more readily so on boiling, and separates well in very pale yellow stars made up of elongated, rhombic plates. It melts at 118—120° and is remarkably sparingly soluble even in boiling methyl alcohol, from which it crystallises as a pale lemon-yellow powder consisting of small, glistening prisms. The crystals are coloured crimson by concentrated nitric acid, partly dissolve, and the addition of water gives an ochreous precipitate. When sulphuric acid is added to the solution of a trace of the substance in glacial acetic acid, a brown coloration is obtained, which is intensified by the addition of a drop of dilute nitric acid.

The *semicarbazone*, $C_{21}H_{23}O_5N_3$, was prepared by boiling the substance with much alcohol and excess of semicarbazide hydrochloride and sodium acetate, when solution took place readily, and, on evaporation to dryness, a crystalline mass remained. This was triturated with water, collected, washed well, and crystallised from methyl alcohol:

0·1027 gave 0·2376 CO_2 and 0·0570 H_2O. C=63·1; H=6·1.
0·1239 ,, 9·7 c.c. N_2 at 17° and 752 mm. N=10·6.
$C_{21}H_{23}O_5N_3$ requires C=63·5; H=5·8; N=10·6 per cent.

This *semicarbazone* melts and effervesces at about 218—220° and is sparingly soluble in boiling methyl alcohol, from which it separates in nodular masses.

Reduction of Oxyberberine to Tetrahydroanhydroberberine,



The main difficulty in carrying out this reduction is the sparing solubility of oxyberberine in dilute acids or in organic solvents, but ultimately the following conditions were found to give the desired result.* Oxyberberine (10 grams), suspended in alcohol (260 c.c. of 97 per cent.), is gradually mixed with sulphuric acid (130 c.c. of 97 per cent.), when the heat generated brings about complete solution and there is no separation of oxyberberine on keeping. The electrolytic cell consisted of a glass jar 20 cm. high

* I am indebted to Mr. G. R. Clemo for assistance in carrying out this reduction.

and of 1 litre capacity; the cathode was a sheet of lead which just fitted round the inside of the glass jar, and, previous to the experiment, had been coated with a layer of electrolytic lead. The anode was a strip of lead, and this was placed in a porous cell, 5 cm. in diameter, containing dilute sulphuric acid (20 per cent.), which was replenished from time to time during the experiment. In carrying out the reduction, the solution, prepared as described above, was placed in the cathodic compartment and a current of about 6 amperes passed for forty-eight hours. The pale yellow product was mixed with ice and water (about 500 grams), allowed to remain for twenty-four hours, and then filtered. The rather considerable grey precipitate (5·3 grams) is largely soluble in hot glacial acetic acid, and, after filtering, the solution deposits oxyberberine acetate (1·5 grams). The portion insoluble in acetic acid (0·8 gram) melts above 300°, and was not further examined. The filtrate from the grey precipitate gives with excess of ammonia a dark-coloured precipitate (4·6 grams), which is collected, dried, and digested with a little methyl alcohol, when much of the dark impurity dissolves and a much cleaner product is left. This is dissolved in boiling, very dilute hydrochloric acid with the addition of animal charcoal and concentrated, when, on keeping, a deep ochreous, crystalline precipitate separates in quantity. The hydrochloride is collected, recrystallised from boiling glacial acetic acid, and the colourless salt decomposed by ammonia. Finally, the base is twice crystallised from acetone, from which it separates in colourless, glistening leaflets. (Found: C=70·6; H=6·2. $C_{20}H_{21}O_4N$ requires C=70·8; H=6·2 per cent.)

This substance melted at 170—171°, and a careful examination both of the base and of its salts clearly established the identity with tetrahydroanhydroberberine (m. p. 170—171°). Moreover, a mixture of the substance with tetrahydroanhydroberberine melted at 170—171°.

The author is much indebted to Mr. Fred Hall for carrying out the analyses given in this paper.

THE UNIVERSITY CHEMICAL LABORATORIES,
OXFORD. [*Received, August* 17*th*, 1918.]

LXVI.—*Morindone.*

By JOHN LIONEL SIMONSEN.

DURING the past few years, owing to the shortage of synthetic dyes, the use of natural colouring matters has, to some extent, been revived, and it appeared, therefore, to be a matter of some interest to attempt to elucidate the constitution of the main constituent of *Morinda citrifolia* and *M. umbellata*, morindone, since the root bark of this tree at one time found considerable application in India for the dyeing of cloth.

Morindone occurs in the root bark mainly in the form of the glucoside, morindin, although a small quantity of the free colouring matter is present in the bark. Morindin appears to have been first isolated from *M. citrifolia* by Anderson (*Annalen*, 1849, **71**, 216). He ascribed to it the formula $C_{28}H_{30}O_{15}$, and by sublimation obtained a substance resembling alizarin in its properties, to which he gave the name morindone. Subsequent investigators appear to have regarded morindin as identical with ruberythric acid and morindone as identical with alizarin. Thorpe and Greenall (T., 1887, **51**, 52), and later Thorpe and Smith (T., 1888, **53**, 171), using *M. citrifolia* as the source of their material, proved conclusively, however, that morindone possessed the formula $C_{15}H_{10}O_5$, and were of the opinion that morindin was more correctly represented by the formula $C_{26}H_{28}O_{14}$ than by the formula suggested by Anderson. They further considered morindone to be a trihydroxymethylanthraquinone.

The presence of morindin and morindone in *M. umbellata* was first proved by Perkin and Hummel (T., 1894, **65**, 851) in their investigation of the constituents of the root bark of this tree. They confirmed the formula $C_{26}H_{28}O_{14}$ (with eight hydroxy-groups) for morindin, and they further showed that in all probability morindone was a trihydroxymethylanthraquinone derived from 2-methylanthraquinone, since, when distilled with zinc dust, 2-methylanthracene was obtained.

Subsequently, Oesterle and Tisza (*Arch. Pharm.*, 1907, **245**, 534) investigated once more the constituents of *M. citrifolia*. They drew the conclusion that morindin from that source had the formula $C_{27}H_{30}O_{15}$ and contained nine hydroxy-groups. They based this conclusion on an analysis of morindin, its acetyl and benzoyl derivatives, and on a quantitative determination of the products of hydrolysis. The properties of the morindin obtained by these authors, and also those of its derivatives, are at distinct

variance with those described by Perkin and Hummel (*loc. cit.*). Perkin (P., 1908, **24**, 150) directed attention to these discrepancies and published further analyses in support of his formula for morindin from *M. umbellata*, and suggested that the morindin derived from *M. umbellata* and *M. citrifolia* might be different.

With regard to the constitution of morindone, beyond the fact that it possesses the formula $C_{15}H_{10}O_5$, contains three hydroxy-groups, and yields 2-methylanthracene on distillation with zinc dust, little is known. Perkin (Thorpe's "Dictionary of Applied Chemistry," III, 547) has suggested either that morindone might be a methylanthragallol or that it might contain a $\cdot CH_2 \cdot OH$ group, the presence of such a group having been suggested by Robinson and Simonsen (T., 1909, **95**, 1088) to explain the relationship between aloe–emodin and rhein, since, as he pointed out, the colour reactions of morindone are somewhat remarkable.

For the preparation of the morindin and morindone required for the experiments described in this paper, the author has used the root bark of *M. citrifolia*, which was obtained for him by Dr. J. R. Henderson, of the Madras Museum, and Mr. Y. Narasihman, lecturer in chemistry, Maharaja's College, Vizianagram, and a considerable quantity of the bark was very kindly extracted for him by Drs. Fowler and Watson at the Indian Institute of Science, Bangalore. The author wishes to take this opportunity of expressing his thanks to these gentlemen.

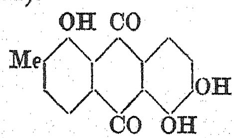
The morindin was extracted and purified essentially by the methods used by Perkin and Hummel, and it is not necessary to describe them in detail. In view of the discrepancies between the work of Perkin and Hummel and that of Oesterle and Tisza mentioned above, a specimen of morindin was very carefully purified by repeated crystallisation from 75 per cent. alcohol, when it was obtained in voluminous, yellow needles which, when rapidly heated, melted at 250—251°; when slowly heated, it sintered at 235° and melted at 245°. (Oesterle and Tisza state that it commenced to sublime at 235° and melted at 245°. Perkin and Hummel do not give a melting point.) The analytical data agreed well with the formula $C_{26}H_{28}O_{14}$ suggested by Perkin. The acetyl derivative was also prepared, and was found to melt at 239—240°. (Oesterle and Tisza give 236°, Perkin 246—248°.) As stated by Perkin, it is very sparingly soluble in cold alcohol, somewhat more readily so in the hot solvent, and contains eight acetyl groups. There would therefore appear to be no difference between the morindin derived from *M. citrifolia* and *M. umbellata*, and the discrepancies between the results of Perkin and Hummel and those of Oesterle and Tisza must be ascribed to some other cause. The author had

hoped to make a direct comparison of the morindins obtained from these two sources, but up to the present he has not succeeded in obtaining a specimen of the root bark of *M. umbellata*.

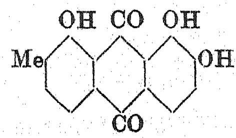
Attempts to isolate in a pure state the sugar formed by the hydrolysis of morindin were unsuccessful. The phenylosazone was prepared, but was found to be a mixture.

The Constitution of Morindone.

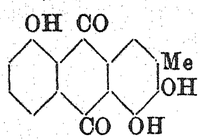
From a consideration of the experiments described in this paper and from the results obtained by previous investigators, the author would suggest that morindone is best represented either as a hydroxymethylanthrarufin (I) or as a hydroxymethylchrysazin (II).



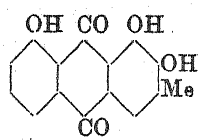
(I.)



(II.)



(III.)



(IV.)

The evidence in support of this view may, perhaps, best be summarised as follows:

(i) The methyl group is in position 2, since morindone on distillation with zinc dust yielded 2-methylanthracene (Perkin and Hummel, *loc. cit.*, p. 856).

(ii) Morindone contains three hydroxy-groups, since it yields triacetyl, tribenzoyl, and trimethoxy-derivatives.

(iii) Two of the hydroxy-groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yielded a monomethyl ether (see p. 773).

(iv) Morindone is a mordant dye resembling alizarin, and hence probably has two of the hydroxy-groups in the 1:2-position.

(v) The hydroxy-group, which undergoes methylation with methyl iodide, must be present in the same ring as another hydroxy-group, since *morindone monomethyl ether* is completely destroyed when oxidised with an alkaline solution of potassium permanganate, only oxalic acid being isolated from the products (see p. 773).

(vi) Morindone cannot be a derivative of anthragallol or purpurin, since it is perfectly stable in alkaline solution and does not undergo oxidation even when air is drawn through such a solution for several days.

(vii) The presence of a $\cdot CH_2\cdot OH$ group, as suggested by Perkin, is unlikely, since all attempts to detect such an alcoholic grouping by oxidation or displacement of the hydroxy-group by a halogen were unsuccessful.

From the above, it follows that the only positions for the hydroxy-groups are as in 1:5:6-trihydroxyanthraquinone or 1:7:8-trihydroxyanthraquinone.

(viii) It is suggested that the methyl group must be in the ortho-position with respect to one of the hydroxy-groups, since all attempts to oxidise it to a carboxyl group by means of chromic acid have proved unsuccessful, the molecule being completely destroyed when once attacked by the oxidising agent. As is well known, *o*-xylene cannot be oxidised to phthalic acid by means of chromic acid, and the author has further found that whereas *p*-tolyl methyl ether when oxidised by means of chromic acid in acetic acid solution gave an excellent yield of anisic acid, *o*-tolyl methyl ether under similar conditions did not yield a trace of the corresponding *o*-methoxy-acid.

(ix) If the view be accepted that the methyl group is in the ortho-position with respect to one of the hydroxy-groups, then four formulæ derived from hydroxyanthrarufin or hydroxychrysazin become possible (I, II, III, and IV). The author would reject formulæ III and IV, since it is highly improbable that substances possessing these formulæ would be methylated by methyl iodide, owing to steric hindrance.

(x) In deciding between formulæ I and II, it would appear that formula I is the more probable, since in its colour reactions morindone resembles more closely hydroxyanthrarufin than hydroxychrysazin. Hydroxyanthrarufin dissolves in sulphuric acid with a violet colour which, on the addition of boric acid, becomes blue; morindone dissolves in sulphuric acid with a blue colour, which is not changed on the addition of boric acid; moreover, the sulphuric–boric acid solutions of hydroxyanthrarufin and morindone are practically indistinguishable in colour. Hydroxychrysazin, on the other hand, dissolves in sulphuric acid with a red colour, which becomes purple on the addition of boric acid. The bluer shades exhibited by morindone are explained by the presence of the methyl group, since, as is well known, methylalizarin yields bluer shades than does alizarin.

Many experiments were made with the object of confirming the

formula suggested above for morindone, but up to the present without success. Morindone trimethyl ether was found to be extremely resistant to oxidising agents. It was only slowly attacked by an alkaline solution of potassium permanganate even in boiling solution. Experiments involving the use of either chromic acid or nitric acid gave only negative results.

The synthesis of morindone is being attempted, but the problem seems to be a difficult one.

EXPERIMENTAL.

Morindin.

The material, isolated and crystallised as described on p. 767 (Found: C=55·3; H=4·9. $C_{26}H_{28}O_{14}$ requires C=55·3; H=4·9 per cent.), was hydrolysed with an alcoholic solution of sulphuric acid, when 0·7556 gave 0·3632 morindone. Yield of morindone = 48·1 per cent., whereas if the formula for morindin were $C_{26}H_{28}O_{14}$, the yield of morindone should be 48·0 per cent.

Acetylmorindin.—This substance was readily prepared by boiling morindin with acetic anhydride containing a trace of pyridine for two hours. It separated from dilute acetic acid in pale sulphur-yellow needles, which melted at 239—240°. For analysis it was dried at 120° (Found: C=56·1; H=5·1. $C_{42}H_{44}O_{22}$ requires C=56·0; H=4·9 per cent.). The number of acetyl groups present was determined by A. G. Perkin's method, and was found to be eight. 0·2074 gave 0·1103 $C_2H_4O_2$, whence Ac=38·2, whereas this amount of a substance of the formula $C_{26}H_{20}O_{14}(Ac)_8$ should yield 0·1106 $C_2H_4O_2$, Ac=38·2 per cent.*

Morindone.

The morindone required for these experiments was obtained from morindin by hydrolysis with an alcoholic solution of sulphuric acid. After crystallisation from toluene, it melted at 275°, and showed all the properties ascribed to this substance (Found: C=66·4; H=3·7. Calc.: C=66·7; H=3·7 per cent.). Morindone was not attacked when heated with an acetic acid solution of hydrogen bromide (saturated at 0°) for some hours at 100° in a sealed tube, nor was it found to be altered when air was drawn through an alkaline solution for some days.

Acetylmorindone.—Acetylmorindone was prepared by heating morindone for two hours with acetic anhydride and anhydrous

* Oesterle and Tisza's formula $C_{27}H_{21}O_{15}(Ac)_9$ requires Ac=39·8 per cent.

sodium acetate. It was purified by crystallisation from acetic acid, when it was obtained in pale yellow needles melting at 249° and commencing to sinter slightly at 243°. This melting point is considerably higher than that given by Perkin and Hummel (*loc. cit.*, p. 856), who state that acetylmorindone melts at 222°. I am, however, informed by Prof. Perkin that this value for the melting point is probably due to a misprint.

For analysis, a specimen was dried at 120°:

0·1129 gave 0·2645 CO_2 and 0·0427 H_2O. C=63·8; H=4·2.

$C_{21}H_{16}O_8$ requires C=63·6; H=4·0 per cent.

Acetylmorindone was not readily attacked by chromic acid, and all attempts to oxidise the methyl group by this reagent were unsuccessful. Thus, when treated with the quantity of chromic acid calculated to oxidise the methyl group to a carboxyl group, a portion of the substance appeared to undergo complete destruction, the remainder being unattacked. A careful examination of the chromic acid solution failed to reveal the presence of any derivative of phthalic acid. When treated with an acetic acid solution of hydrogen bromide (saturated at 0°) in a sealed tube at 100°, hydrolysis of the acetyl derivative took place, but no trace of a halogen derivative was formed, as would in all probability have been the case if a $\cdot CH_2 \cdot OAc$ group had been present (compare Perkin and Simonsen, T., 1904, **85**, 854; Müller, T., 1907, **91**, 1782).

Benzoylmorindone.—Morindone (1 gram) was mixed with pyridine (5 c.c.), and, after cooling in ice, benzoyl chloride (2 grams) was gradually added. The reaction proceeded readily, and, after remaining for thirty minutes, the mixture was poured into water, when a viscid oil separated, which rapidly solidified on triturating with hot alcohol. It was crystallised from acetic acid, when it was obtained in nodules of fine, yellow needles melting at 218—219°. For analysis, it was dried at 120°:

0·1079 gave 0·2924 CO_2 and 0·0403 H_2O. C=73·9; H=4·1.

$C_{36}H_{22}O_8$ requires C=74·2; H=3·8 per cent.

Methylation of Morindone: Morindone Monomethyl Ether and Trimethyl Ether.

Many experiments were made with a view to devise a satisfactory method for the preparation of morindone trimethyl ether. It was ultimately found that the following somewhat laborious process gave the best results.

Morindone (3 grams) was mixed with a solution of potassium

hydroxide (12 grams) dissolved in water (15 c.c.) and treated with methyl sulphate (15 c.c.), which was added all at once. The mixture was vigorously stirred, and when the reaction was complete, the same quantities of alkali and methyl sulphate were added. The alkaline solution, which was now deep red, was boiled, acidified, the crude methylation product collected, and again treated with alkali and methyl sulphate as before. The red solution contained in suspension a deep red, sparingly soluble potassium salt and the yellow trimethyl ether. It was filtered through cloth, and the residue boiled with dilute alkali and filtered, this treatment being repeated three times, when the filtrate should only be slightly red. The residue was ground with a considerable volume of chloroform, which dissolved the morindone trimethyl ether, leaving the insoluble, red potassium salt of the monomethyl ether *A* (see p. 773). The chloroform extract was evaporated, the crude, pale yellow trimethyl ether dissolved in hot toluene, and the toluene solution repeatedly washed with hot dilute alkali, which removed a further quantity of partly methylated morindone. (The alkaline washings were mixed with *A*.)

After separating from the alkali, the toluene solution was filtered, the toluene removed in a current of steam, when the nearly pure trimethyl ether was obtained. It was crystallised from acetic acid, when it separated in pale yellow needles melting at 229°, as stated by Oesterle and Tisza:

0·1013 gave 0·2566 CO_2 and 0·0426 H_2O. C=69·1; H=4·7.
$C_{18}H_{16}O_5$ requires C=69·2; H=5·1 per cent.

Morindone trimethyl ether, when pure, is insoluble in alkali; in sulphuric acid it dissolves to a deep blue solution.

The oxidation of morindone trimethyl ether has been carefully investigated. The ether was found to be extremely stable to chromic acid, and the greater part was recovered unchanged when oxidised with the equivalent quantity of oxidising agent, the remainder being apparently completely destroyed. When suspended in dilute sodium carbonate solution and boiled with a solution of potassium permanganate for several days, it was slowly oxidised. Much of the ether remained unattacked, and, with the exception of oxalic acid, no acid could be isolated in sufficient quantity for identification. When nitric acid was used as the oxidising agent, only oxalic acid appeared to be formed.

The sparingly soluble red potassium salt *A*, mentioned above, was suspended in hot water, decomposed with hydrochloric acid, and the brown solid which separated was collected. It was purified

by repeated crystallisation from acetic acid. For analysis, it was dried at 120°:

0·1012 gave 0·251 CO_2 and 0·0388 H_2O. C=67·6; H=4·2.
0·1028 ,, 0·2561 CO_2 ,, 0·038 H_2O. C=67·9; H=4·1.
$C_{16}H_{12}O_5$ requires C=67·6; H=4·2 per cent.

Morindone monomethyl ether crystallises in iridescent, brown needles melting at 248°. It is readily soluble in chloroform, toluene, or hot acetic acid, more sparingly so in ether or ethyl acetate, and very sparingly so in alcohol. It dissolves in concentrated sulphuric acid with a colour similar to that shown by morindone, only slightly redder. The sulphuric acid solution on the addition of a crystal of potassium nitrate gives a fine, greenish-red coloration. In fuming nitric acid, it dissolves with a transient red colour, yielding almost immediately a reddish-brown solution. It forms sparingly soluble red sodium and potassium salts, the solutions of which exhibited a slight fluorescence reminiscent of eosin. An attempt was made to determine the number of methoxy-groups present by the ordinary Zeisel method, but owing to the sparing solubility of the substance, the results were always low, although the heating was continued for from four to five hours and the hydriodic acid was mixed with acetic anhydride. Morindone monomethyl ether is readily attacked by an alkaline solution of potassium permanganate; it appears to undergo complete disintegration, and the bearing of this fact on the determination of the constitution of morindone has already been discussed.

Morindone monomethyl ether was also prepared by treating morindone with methyl iodide in the presence of sodium methoxide. Morindone (0·5 gram) was mixed with sodium methoxide (1·3 grams of sodium), and, after the addition of methyl iodide (0·8 gram), the mixture was heated in a sealed tube at 100° for eight hours. The deeply coloured product was poured into water, and, after the addition of potassium hydroxide solution, was boiled, filtered, and the residual potassium salt well washed with hot dilute alkali until the washings were only faintly coloured. The salt was decomposed with dilute hydrochloric acid, and the brown solid thus obtained (0·1 gram) was collected and recrystallised from acetic acid, when it melted at 247—248° and showed all the properties of morindone monomethyl ether. The melting point was not altered on admixture with an equal amount of the monomethyl ether prepared by means of methyl sulphate, as described above.

Diacetylmorindone Monomethyl Ether.—This substance was

readily prepared when the monomethyl ether was heated for two hours with acetic anhydride and anhydrous sodium acetate. It was crystallised from acetic acid and dried at 120° for analysis:

0·1042 gave 0·2494 CO_2 and 0·041 H_2O. C = 65·3; H = 4·3.

$C_{20}H_{15}O_7$ requires C = 65·2; H = 4·3 per cent.

Diacetylmorindone monomethyl ether separates from acetic acid in yellow, hexagonal prisms melting at 245—246°. It is sparingly soluble in hot alcohol.

The Sugars from Morindin.

In one experiment, the acid mother liquor from which the morindone had been separated was treated with sodium acetate until the excess of mineral acid was neutralised, and the solution concentrated to a small bulk. Excess of phenylhydrazine was added, and, after heating on the water-bath for one hour, the brownish-yellow osazone was collected. After repeated fractional crystallisation from alcohol, a sparingly soluble fraction was obtained which separated in fine yellow needles decomposing at 207°:

0·0689 gave 11 c.c. N_2 at 30° and 760 mm. N = 17·2.

$C_{17}H_{20}O_3N_4$ requires N = 17·1 per cent.

This substance would, therefore, appear to be the osazone of a pentose, and is possibly identical with the osazone (m. p. 202—203°) described by Perkin (*loc. cit.*, p. 150), but owing to the small quantity of material which was obtained in a pure state, great trust cannot be placed in the result of the analysis. From the mother liquor from which the above-mentioned osazone had been separated, a small quantity of another osazone was isolated, in stout yellow needles, which melted at about 195° and were readily soluble in alcohol.

The author wishes to thank Mr. M. Gopala Rau, M.A., for the care with which he made the analyses required for this and the following communication.

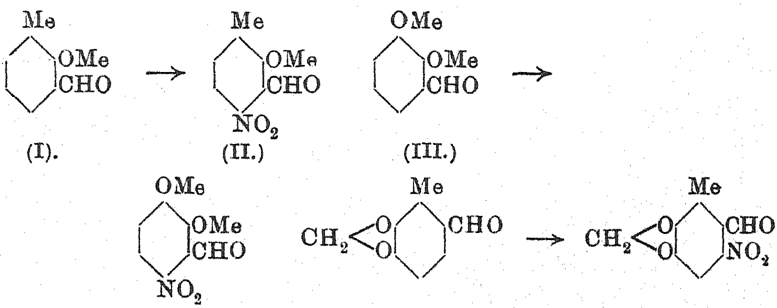
THE PRESIDENCY COLLEGE,
MADRAS.

[*Received, May* 16*th*, 1918.]

LXVII.—*The Nitration of 2- and 6-Methoxy-*m-*Tolualdehydes and* m-*Toluic Acids.*

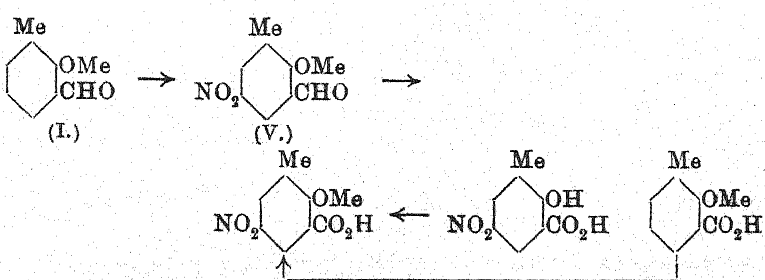
By John Lionel Simonsen.

For synthetical experiments in the anthraquinone group, the author was desirous of preparing 3-methoxy-4-methylphthalic acid, and it appeared probable that the simplest method would be by nitrating *2-methoxy-*m-*tolualdehyde* (I), when it was expected that the nitro-group would enter the ortho-position with respect to the aldehyde group with the formation of 4-nitro-2-methoxy-*m*-tolualdehyde (II), which could then be readily converted into the required acid, for it has been shown that *o*-veratraldehyde (III) and 5:6-methylenedioxy-*o*-tolualdehyde (IV), on nitration, yield nitro-derivatives containing the nitro-group in the ortho-position with respect to the aldehyde group (Perkin and Robinson, T., 1914, **105**, 2389; Perkin, T., 1916, **109**, 910).



(I). (II.) (III.) (IV.)

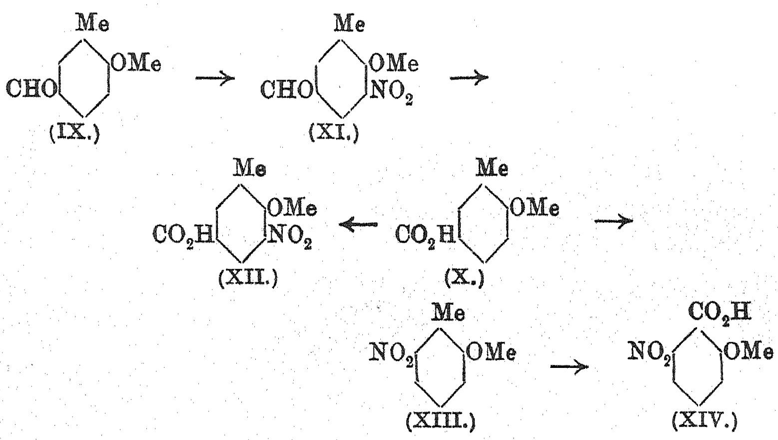
This expectation was not, however, realised, for when 2-methoxy-*m*-tolualdehyde was treated with nitric acid under the conditions described in the experimental part of this paper (see p. 778), an almost quantitative yield of *5-nitro-2-methoxy-*m-*tolualdehyde* (V) was obtained.



(I.) (V.) (VI.) (VII.) (VIII.)

The constitution of this aldehyde was readily proved by the fact that on oxidation it was converted into 5-*nitro-2-methoxy-m-toluic acid* (VI), an acid which was readily obtained by the methylation of 5-nitro-2-hydroxy-*m*-toluic acid (VII) (Einhorn and Pfyl, *Annalen*, 1900, **311**, 47; Fortner, *Monatsh.*, 1901, **22**, 939).

5-Nitro-2-methoxy-*m*-toluic acid was also prepared by the nitration of 2-*methoxy-m-toluic acid* (VIII), which was obtained by the oxidation of the aldehyde.



During the preparation of the 2-hydroxy-aldehyde, a considerable quantity of the 6-hydroxy-aldehyde was obtained, and it appeared, therefore, to be of some interest to investigate the nitration of 6-methoxy-*m*-tolualdehyde (IX) and 6-methoxy-*m*-toluic acid (X). The aldehyde on nitration gave an excellent yield of the 5-*nitro*-derivative (XI), the constitution of which was proved by the fact that on treatment with acetone and alkali it yielded the corresponding derivative of distyryl ketone, no formation of indigotin taking place, which would have been the case if the nitro-group had entered either of the positions ortho to the aldehyde group. The nitro-aldehyde yielded on oxidation the corresponding *acid* (XII), which acid was also formed by the nitration of 6-methoxy-*m*-toluic acid.

At the same time, there was obtained a considerable quantity of a neutral substance melting at 69°, which would appear to be 6-*nitro-o-tolyl methyl ether* (XIII). As was to be expected of a substance possessing this constitution, some difficulty was experienced in converting the methyl group into a carboxyl group. This was ultimately accomplished by oxidation with chromic acid in concentrated sulphuric acid solution, when an acid was obtained crystallising in prismatic needles and melting at 161°. Simonsen and

Rau (T., 1916, **111**, 223 *et seq.*) have described three of the four possible isomeric nitro-2-methoxybenzoic acids; this acid was found not to be identical with any of the three, and it is in all probability 6-*nitro-2-methoxybenzoic acid* (XIV). Unfortunately, it was not obtained in sufficient quantity for a detailed examination to be made.

The results described above are of some interest in illustrating the difference in orientating effect of methyl and methoxy-groups. It has been suggested (Simonsen and Rau, *loc. cit.*) that a negative group in the ortho-position with respect to a positive group tends to neutralise such a grouping, and the orientating effect is then in the main exercised by the remaining positive group in the molecule. Whilst this appears to be the case in the nitration of acetylamino-methoxy-derivatives and also of other methoxy-derivatives, the rule is evidently not of any general application.

EXPERIMENTAL.

2-*Methoxy*-m-*tolualdehyde* (I).

The phenolic aldehyde (10 grams) was dissolved in sodium methoxide (2 grams of sodium) and treated with methyl sulphate (15 grams), the addition of the same quantities of alkali and methyl sulphate being repeated three times. The solution was then heated on the water-bath for fifteen minutes to complete the decomposition of the methyl sulphate, water added, the methoxy-aldehyde extracted with ether, and the ethereal solution dried and evaporated.

2-*Methoxy*-m-*tolualdehyde* was obtained as a viscid, pleasant-smelling oil which boiled at about 120°/6 mm. With concentrated sulphuric acid it gave a cherry-red coloration.

The *oxime* was best prepared by dissolving the aldehyde (1·3 grams) in alcohol, and, after the addition of hydroxylamine hydrochloride (2 grams) and sodium acetate (2 grams), the mixture was heated on the water-bath for half an hour. On pouring into water, the oxime separated in silky needles, which were purified by crystallisation from methyl alcohol. It melted at 118°:

0·1558 gave 12·9 c.c. N_2 at 33° and 759 mm. N=8·7.

$C_9H_{11}O_2N$ requires N=8·5 per cent.

The *semicarbazone*, prepared in the usual manner, crystallised from alcohol, in which it was somewhat sparingly soluble, in white, microscopic needles melting at 224°:

0·0906 gave 16·8 c.c. N_2 at 30° and 760 mm. N=20·0.

$C_{10}H_{13}O_2N_3$ requires N=20·2 per cent.

Nitration of 2-Methoxy-m-tolualdehyde. 5-Nitro-2-methoxy-m-tolualdehyde (V).

In one experiment, the aldehyde (2 grams) was added gradually to nitric acid (D 1·52 : 10 grams), which was kept well cooled in ice. The reaction proceeded smoothly, and, after remaining for fifteen minutes, the mixture was poured on ice, when an oil separated which rapidly solidified. This was collected, triturated with dilute sodium carbonate solution * to remove a trace of acid, dried on porous porcelain, and purified by crystallisation from a mixture of ether and light petroleum (yield, 2·2 grams):

0·1634 gave 10·7 c.c. N_2 at 30° and 759 mm. N = 7·0.
$C_9H_9O_4N$ requires N = 7·2 per cent.

5-*Nitro-2-methoxy-m-tolualdehyde* crystallises in balls of needles melting at 61—62°. It is readily soluble in the ordinary organic solvents with the exception of light petroleum, in which it is somewhat sparingly soluble. The 5-nitro-aldehyde was found to be the sole product of the reaction, since no trace of an isomeride could be isolated from the mother liquors.

The *semicarbazone* crystallised from alcohol in fine, woolly needles which decomposed at 233°:

0·0948 gave 19·4 c.c. N_2 at 32° and 758 mm. N = 22·0.
$C_{10}H_{12}O_4N_4$ requires N = 22·2 per cent.

5 : 5′-*Dinitro-2 : 2′-dimethoxydi-3-m-methylstyryl Ketone*,
$NO_2\cdot C_6H_2Me(OMe)\cdot CH:CH\cdot CO\cdot CH:CH\cdot C_6H_2Me(OMe)\cdot NO_2$.

This substance was readily prepared under the following conditions: the aldehyde (0·5 gram), dissolved in warm methyl alcohol (5 c.c.), was mixed with acetone (0·5 gram), and, after the addition of potassium hydroxide (50 per cent. : two drops), the yellow mixture was heated to boiling for a few minutes. The liquid rapidly clouded and a voluminous mass of yellow needles separated. These were collected, well washed with methyl alcohol, and the residue recrystallised from acetic acid, in which it was only very sparingly soluble, when it was obtained in fine, yellow needles decomposing at 252°:

0·094 gave 6 c.c. N_2 at 32° and 758 mm. N = 6·8.
$C_{21}H_{20}O_7N_2$ requires N = 6·8 per cent.

* The acid (0·05 gram) which separated from the sodium carbonate solution on acidification was found to be 5-nitro-2-methoxy-*m*-toluic acid.

*Oxidation of 5-Nitro-2-methoxy-*m*-tolualdehyde. 5-Nitro-2-methoxy-*m*-toluic Acid* (VI).

The nitro-aldehyde (1·2 grams) was dissolved in acetone (30 c.c.) and finely powdered potassium permanganate (0·65 gram) was gradually added. The oxidation proceeded readily, and, after the reaction was complete, water was added, the solution boiled, and the manganese dioxide filtered off. The filtrate was concentrated on the water-bath until free from acetone, a trace of unchanged aldehyde removed, and the aqueous solution acidified, when the nitro-acid separated in fine needles. These were collected and crystallised from hot water:

0·2036 gave 12 c.c. N_2 at 30° and 759 mm. N = 6·3.
$C_9H_9O_5N$ requires N = 6·6 per cent.

*5-Nitro-2-methoxy-*m*-toluic acid* crystallises from hot water in glistening, silky needles melting at 154°. It is readily soluble in the ordinary organic solvents with the exception of light petroleum.

The *silver* salt separated in pale yellow needles, which were somewhat soluble in hot water:

0·2974 gave 0·1007 Ag. Ag = 33·8.
$C_9H_8O_5NAg$ requires Ag = 34·0 per cent.

For the purposes of comparison, a specimen of 5-nitro-2-methoxy-*m*-toluic acid was prepared by the methylation of the corresponding hydroxy-acid obtained by the nitration of 2-hydroxy-*m*-toluic acid (Einhorn and Pfyl, *loc. cit.*). The acid isolated from the methylation melted at 154°, and was identical in every way with the acid prepared by the method described above.

*2-Methoxy-*m*-toluic Acid* (VIII).

This acid was readily obtained by the oxidation of the corresponding aldehyde by means of potassium permanganate in acetone solution. It separated from hot water in hair-like needles which melted at 83°. It was readily soluble in hot water and in the ordinary organic solvents, somewhat readily so in cold water:

0·0952 gave 0·2266 CO_2 and 0·053 H_2O. C = 64·9; H = 6·2.
$C_9H_{10}O_3$ requires C = 65·1; H = 6·1 per cent.

The *silver* salt was obtained as a caseous, white precipitate which was dried at 100° for analysis:

0·37 gave 0·1475 Ag. Ag = 39·9.
$C_9H_9O_3Ag$ requires Ag = 39·6 per cent.

Nitration of 2-Methoxy-m-*toluic Acid.*

The acid (0·3 gram) was gradually added to nitric acid (D 1·52: 1 gram), the temperature being kept at about 30°. After remaining for ten minutes, the clear solution was poured into water, when the nitro-acid separated and was collected (yield, 0·3 gram). After crystallisation from hot water, it melted at 154°, and this melting point was unaltered on admixture with a specimen of the 5-nitro-acid prepared by the oxidation of the nitro-aldehyde as described above. The 5-nitro-acid appeared to be the sole product of the reaction, since the mother liquors yielded no trace of an isomeride.

Nitration of 6-Methoxy-m-*tolualdehyde* (IX). *5-Nitro-6-methoxy*-m-*tolualdehyde* (XI).

The aldehyde (3 grams) was added slowly to nitric acid (D 1·52: 9 grams), which was kept well cooled in a mixture of salt and ice. The aldehyde dissolved with considerable evolution of gas, and, after remaining for ten minutes, the mixture was poured on ice, when the nitro-aldehyde separated and was collected (yield, 4·2 grams).

5-*Nitro-6-methoxy*-m-*tolualdehyde* crystallises from dilute alcohol in small needles melting at 77°. It is readily soluble in all the ordinary organic solvents:

0·1093 gave 7·2 c.c. N_2 at 31° and 760 mm. N=7·1.

$C_9H_9O_4N$ requires N=7·2 per cent.

The *semicarbazone* crystallised from alcohol in needles which decomposed at 235°:

0·0849 gave 17·4 c.c. N_2 at 31° and 760 mm. N=22·0.

$C_{10}H_{12}O_4N_4$ requires N=22·2 per cent.

5:5′-*Dinitro*-4:4′-*dimethoxydi*-3-*methylstyryl Ketone.*

This substance was prepared in a similar manner to the isomeride described on p. 778. It crystallises from acetic acid in yellow needles melting at 214°:

0·0526 gave 3·4 c.c. N_2 at 30° and 759 mm. N=6·9.

$C_{21}H_{20}O_7N_2$ requires N=6·8 per cent.

5-*Nitro-6-methoxy*-m-*toluic Acid* (XII).

This acid was readily obtained when the nitro-aldehyde was oxidised with potassium permanganate in acetone solution. For analysis, it was crystallised from dilute alcohol:

0·1752 gave 11·2 c.c. N_2 at 31° and 760 mm. N=6·8.

$C_9H_9O_5N$ requires N=6·6 per cent.

5-*Nitro*-6-*methoxy*-m-*toluic acid* crystallises in colourless, felted needles melting at 180—181°, and softening slightly at 175°. It is very sparingly soluble in cold water, somewhat more readily so in hot; it is very readily soluble in chloroform, acetic acid, or ethyl acetate, more sparingly so in benzene.

The *barium* salt crystallised in sparingly soluble, curious nodular masses of needles; the *calcium* salt was obtained in stellate clusters of needles which were readily soluble in hot water; the *silver* salt separated as a granular, white precipitate:

0·2272 gave 0·0772 Ag. Ag=34·0.

$C_9H_8O_5NAg$ requires Ag=34·0 per cent.

The *methyl* ester, $C_{10}H_{11}O_5N$, crystallised from dilute methyl alcohol in silky needles melting at 47°.

Nitration of 6-*Methoxy*-m-*toluic Acid* (X).

The finely powdered acid (1·4 grams) was gradually added to nitric acid (D 1·52 : 5 grams), the temperature being kept between 30° and 35°. The acid dissolved with considerable evolution of gas, and, after remaining for ten minutes, the mixture was poured into water and the solid which separated was collected and triturated with dilute sodium carbonate solution, a considerable quantity of a neutral substance, *A* (0·62 gram), remaining undissolved. This was separated, the filtrate acidified, and the acid which was deposited (0·97 gram) crystallised from dilute alcohol, when it was obtained in fine needles melting at 180—181°, this melting point being unaltered on admixture with a specimen of the acid obtained by the oxidation of the nitro-aldehyde. The neutral substance *A* was purified by crystallisation from methyl alcohol, from which it separated in glistening needles melting at 69°. For analysis, it was dried in a vacuum:

0·1404 gave 11 c.c. N_2 at 30° and 759 mm. N=8·5.

$C_8H_9O_3N$ requires N=8·4 per cent.

This substance would appear to be 6-*nitro*-o-*tolyl methyl ether* (XIII). It was attacked by a hot alkaline solution of potassium permanganate only with great difficulty, but it was found to be readily oxidised by chromic acid under the following conditions: the nitro-compound (0·25 gram) was dissolved in concentrated sulphuric acid (1 c.c.) and gradually treated with chromic acid (0·3 gram) dissolved in concentrated sulphuric acid (2 c.c.), the temperature being kept at about 40°. When the reaction was

complete, water was added, the nitro-acid which separated was collected, dissolved in a little dilute sodium carbonate solution, and filtered from a little unattacked material. On acidifying the alkaline filtrate, the *nitro-acid* separated in fine, prismatic needles which melted at 159—160°. After crystallisation from hot water, in which it was readily soluble, it melted at 161°. This acid was probably *6-nitro-2-methoxybenzoic acid* (XIV), an acid which does not appear to have been described previously. It was not identical with 5-nitro-2-methoxybenzoic acid, which also melts at this temperature (Simonsen and Rau, T., 1917, **111**, 228), since a mixture of the two acids melted at about 140°. Unfortunately, this new acid was not obtained in sufficient quantity for a detailed examination.

In conclusion, the author wishes to thank Mr. M. Gopala Rau, M.A., for his assistance in the analytical work.

THE PRESIDENCY COLLEGE,
MADRAS.

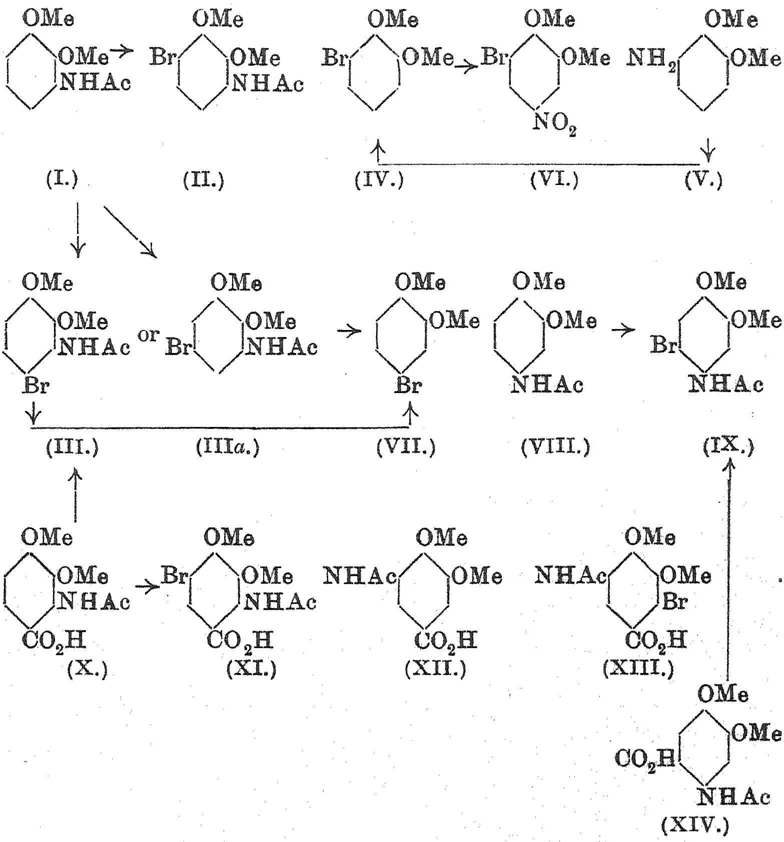
[*Received, May 16th 1918.*]

LXVIII.—*The Bromination of some Derivatives of Veratrole.*

By JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU.

IN previous communications (T., 1917, **111**, 69, 220; this vol., p. 22), the results of experiments were described on the nitration of some acetylamino-derivatives of veratrole and methoxybenzoic acids, and attention was directed to the relative orientating influence of methoxy-groups having positive or negative groups in the ortho- or para-positions. In continuation of these experiments, it appeared to us to be a matter of some interest to investigate the effect of bromination on the same series of compounds in order to determine whether substitution would proceed similarly. When these experiments were nearing completion, a paper by Jones and Robinson (T., 1917, **111**, 903) appeared which has anticipated our work in some directions.

We selected for our experiments the two isomeric acetylaminoveratroles and the three acetylaminoveratric acids, and the results obtained are shown diagrammatically below.



The bromination was performed either in chloroform or in glacial acetic acid solution, the sparingly soluble bromo-amide which separated was decomposed with water, and the product isolated in a suitable manner. As will be observed, the bromine always entered the nucleus in the para-position with respect to the acetylamino-group, except in the case of 6-acetylaminoveratric acid (XIV), when, this position being already occupied, the carboxyl group was eliminated with the formation of 5-bromo-4-acetylaminoveratrole (IX). Only in one case was the formation of an isomeride detected, namely, when 3-acetylaminoveratrole (I) was brominated under special conditions (see p. 786). It has not, unfortunately, proved possible to orientate this isomeride, which must be either the 4- or 5-bromo-derivative (III or IIIa), since on the elimination of the amino-group it yielded 4-bromoveratrole. From analogy, it is most probably the 4-isomeride, and this view receives

support from the fact that traces of this bromide were also formed during the bromination of 2-acetylaminoveratric acid (X).

The constitution of the main product of the bromination of 3-acetylaminoveratrole, 6-*bromo*-3-*acetylaminoveratrole* (II), was determined by eliminating the amino-group with the formation of 3-*bromoveratrole* (IV), a substance which was also prepared from 3-aminoveratrole (V), the bromide from each source being converted by nitration into 6-bromo-4-nitroveratrole (VI), which has already been described by Jones and Robinson (*loc. cit.*, p. 918).

The bromination of 4-acetylaminoveratrole (VIII) has already been investigated by Jones and Robinson (*loc. cit.*, p. 913), who found that 5-bromo-4-acetylaminoveratrole (IX) was formed. This result we are able to confirm, but we have found that the compound melted at 127—128°, and not at 140° as stated by these authors. In view of the ease with which this substance was obtained in a pure state, it appears to us probable that the melting point quoted by Jones and Robinson is due to a misprint.*

The determination of the constitution of the isomeric bromoacetylaminoveratric acids (XI, XIII) obtained by the bromination of 2- and 5-acetylaminoveratric acids (X, XII) offered no difficulty, the corresponding bromoveratric acids being obtained on displacement of the amino-group by hydrogen.

In view of the fact that the formation of the bromo-amide always preceded substitution in the nucleus, which was therefore indirect, these experiments cannot be said to have thrown any light on the mechanism of the nitration of this type of substance. If indirect substitution directed by the methoxy-group does take place on nitration, it should prove possible by choice of suitable conditions to isolate this salt, and it is hoped to make further experiments with the object of throwing light on this problem.

EXPERIMENTAL.

Bromination of 3-*Acetylaminoveratrole* (I). 6-*Bromo*-3-*acetylaminoveratrole* (II).

In one experiment, 3-acetylaminoveratrole (3 grams) was dissolved in chloroform (9 c.c.), and to the ice-cold solution bromine (2·64 grams) dissolved in chloroform (3 c.c.) was gradually added, when bromination took place readily with the separation of the sparingly soluble yellow bromo-amide. After remaining for fifteen minutes, the precipitate was decomposed by the addition of water, the chloroform solution separated, washed with a little

* Prof. Robinson has since informed me that this is the case.—J. L. S.

dilute alkali, dried, and evaporated, when a theoretical yield of the bromoacetylamine was obtained. It was purified by crystallisation from dilute acetic acid:

0·1942 gave 0·1332 AgBr. Br = 29·3.

0·1544 „ 7·6 c.c. N_2 at 30° and 758 mm. N = 5·3.

$C_{10}H_{12}O_3NBr$ requires Br = 29·2; N = 5·1 per cent.

6-*Bromo*-3-*acetylaminoveratrole* crystallises in prismatic needles melting at 78°. It is readily soluble in all the ordinary organic solvents with the exception of benzene and light petroleum. The same bromoacetylamine was found to be the sole product when glacial acetic acid was used as the solvent in place of chloroform.

6-*Bromo*-3-*aminoveratrole* was formed when the acetyl derivative was heated on the water-bath for some hours with hydrochloric acid (50 per cent.). It crystallises from dilute methyl alcohol in colourless needles melting at 66°, and is readily soluble in the ordinary organic solvents:

0·119 gave 6·6 c.c. N_2 at 30° and 759 mm. N = 6·0.

$C_8H_{10}O_2NBr$ requires N = 6·0 per cent.

The *benzoyl* derivative crystallised from dilute alcohol in minute, radiating needles melting at 75°:

0·1935 gave 8·0 c.c. N_2 at 30° and 760 mm. N = 4·4.

$C_{15}H_{14}O_3NBr$ requires N = 4·1 per cent.

3-*Bromoveratrole* (IV) *and* 6-*Bromo*-4-*nitroveratrole* (VI).

I. For the determination of the constitution of the bromo-amide described above, it was necessary to prepare 3-*bromoveratrole*. This substance, which does not appear to have been previously described, was readily obtained when 3-aminoveratrole (Gibson, Simonsen, and Rau, *loc. cit.*, p. 79) was diazotised and treated with cuprous bromide in the usual manner. It was purified by distillation in a current of steam and subsequent distillation under diminished pressure, when it was obtained as a somewhat viscid oil boiling at 114°/5 mm.:

0·1287 gave 0·1117 AgBr. Br = 36·9.

$C_8H_9O_2Br$ requires Br = 36·9 per cent.

When 3-bromoveratrole was dissolved in acetic acid and treated with nitric acid (D 1·4), it yielded 6-bromo-4-nitroveratrole, which crystallised from alcohol in needles melting at 112—113°, and was found by direct comparison to be identical with the substance described by Jones and Robinson (*loc. cit.*, p 918) (Found: N = 5·5. Calc.: N = 5·3 per cent.).

II. 3-Bromoveratrole was also formed when 6-bromo-3-amino-

veratrole (see above) was diazotised in alcoholic solution with amyl nitrite in the usual manner. It was identified by conversion into 6-bromo-4-nitroveratrole melting at 112—113° (Found: N = 5·5. Calc.: N = 5·3 per cent.).

4- or 5-*Bromo-3-acetylaminoveratrole* (III or III*a*).

For the preparation of this substance, the following method was found to be the most convenient. The acetylamine (5 grams) was dissolved in acetic acid (50 per cent.: 20 c.c.) and bromine (4·2 grams) was gradually added to the well-cooled solution. When bromination was complete, the mixture was diluted with water and ammonia added until a nearly neutral solution was obtained. On remaining overnight, the bromination product, *A*, separated; this was collected and the filtrate repeatedly extracted with ether. The ether was evaporated and the residual oil triturated with cold acetone, when a sparingly soluble solid remained. This was mixed with the product *A* (see above) and purified by crystallisation from acetone, when it separated in well-defined octahedra melting at 151° (yield, 2 grams):

0·1966 gave 0·136 AgBr. Br = 29·4.
0·1842 ,, 9·4 c.c. N_2 at 30° and 756 mm. N = 5·3.
$C_{10}H_{12}O_3NBr$ requires Br = 29·2; N = 5·1 per cent.

4- or 5-Bromo-3-acetylaminoveratrole is readily soluble in alcohol or acetic acid, more sparingly so in benzene, acetone, ether, or light petroleum.

The corresponding *amine* was obtained by heating the acetyl derivative for one hour on the water-bath with sulphuric acid (50 per cent.). It separated from dilute methyl alcohol in colourless needles melting at 49°:

0·1268 gave 0·1023 AgBr. Br = 34·4.
$C_8H_{10}O_2NBr$ requires Br = 34·4 per cent.

The *benzoyl* derivative, $C_{15}H_{14}O_3NBr$, crystallised from dilute alcohol in needles melting at 146°.

The *platinochloride* separated from dilute hydrochloric acid in aggregates of yellowish-brown prisms which darkened at 200° and gradually decomposed when heated above this temperature:

0·1659 gave 0·0402 Pt. Pt = 24·2.
$(C_8H_{10}O_2NBr)_2H_2PtCl_4$ requires Pt = 24·3 per cent.

When the above-mentioned bromo-amine was diazotised, it yielded 4-bromoveratrole, which was identified by conversion into 4-bromo-5-nitroveratrole melting at 123° (Jones and Robinson,

loc. cit., give 125° as the melting point of this substance (Found: N=5·3. Calc.: N=5·2 per cent.).

The acetone solution from which the 4- or 5-bromo-3-acetylaminoveratrole had been separated was evaporated, and the residue (5·5 grams) was repeatedly crystallised from alcohol, when a substance melting at 78° was isolated and found by direct comparison to be 6-bromo-3-acetylaminoveratrole.

Bromination of 4-Acetylaminoveratrole (VIII). *5-Bromo-4-acetylaminoveratrole* (IX).

As has already been mentioned in the introduction (p. 784), the bromination of 4-acetylaminoveratrole has already been investigated by Jones and Robinson (*loc. cit.*, p. 913), who found that 5-bromo-4-acetylaminoveratrole was formed. We have investigated this bromination both in chloroform and in acetic acid solutions, when the 5-bromo-derivative was obtained as the sole product. It crystallised from hot water in long, slender needles which melted at 127—128°. Attention has already been directed to the discrepancy between this melting point and that found by Jones and Robinson:

0·1981 gave 0·1352 AgBr. Br=29·3.

$C_{10}H_{12}O_3NBr$ requires Br=29·2 per cent.

5-Bromo-4-aminoveratrole, which has not been described previously, was obtained only with considerable difficulty, owing to the ease with which it decomposed. Ultimately, the following method was found to be fairly satisfactory. The bromoacetylamine was dissolved in a methyl-alcoholic solution of potassium hydroxide (15 per cent. KOH) and heated on the water-bath for three hours, the excess of potassium hydroxide removed by carbon dioxide, the solution filtered, and the methyl alcohol evaporated in a vacuum at the ordinary temperature. The residue was extracted with ether, the ether evaporated, when the base was obtained as a viscid oil which rapidly crystallised. After draining on porous porcelain, it was recrystallised from dilute methyl alcohol, from which it separated in colourless needles melting at 51°. When exposed to the air, the base rapidly darkened in colour:

0·0844 gave 0·0682 AgBr. Br=34·4.

$C_8H_{10}O_2NBr$ requires Br=34·4 per cent.

The *benzoyl* derivative, $C_{15}H_{14}O_3NBr$, crystallised in needles melting at 142°.

The constitution of this bromo-amine was readily determined by conversion into 4:5-dibromoveratrole. The bromo-amine (1 gram) was dissolved in hydrobromic acid (30 per cent.: 5 c.c.) and diazo-

tised by the addition of sodium nitrite (0·4 gram). After remaining in the cold for half an hour, the mixture was poured into hydrobromic acid (5 c.c.) containing a little copper powder and allowed to remain in the cold overnight. The solution was warmed on the water-bath, extracted with ether, the ether evaporated, and the residue crystallised from alcohol, when 4:5-dibromoveratrole separated in needles melting at 92°, which melting point was not changed on admixture with a specimen of the compound obtained from a different source.

Bromination of 2-Acetylaminoveratric Acid (X). *5-Bromo-2-acetylaminoveratric Acid* (XI).

I. 2-Acetylaminoveratric acid (2 grams) was suspended in acetic acid (4 c.c.) and mixed with bromine (1·3 grams) dissolved in acetic acid (2 c.c.); the mixture was sealed up and allowed to remain, with occasional shaking, for twenty-four hours, when the colour of the bromine had completely disappeared and a yellow, unstable bromo-amide had separated. On the addition of water, a clear solution was obtained, from which the bromo-acid gradually crystallised. This was collected, and a further quantity obtained by extracting the filtrate with ether (yield, 2·1 grams). On trituration with dilute sodium carbonate solution, a small quantity of a neutral substance (0·1 gram) remained undissolved. This crystallised from alcohol in needles melting at about 168°, but it was not obtained in sufficient quantity for investigation. The acid which separated from the alkaline filtrate on acidification was found to be quite homogeneous, and was purified by crystallisation from ethyl acetate:

0·1534 gave 0·0908 AgBr. Br=25·2.

$C_{11}H_{12}O_5NBr$ requires Br=25·1 per cent.

5-*Bromo-2-acetylaminoveratric acid* separates in fine needles melting at 188—189°. It is readily soluble in acetone, alcohol, ethyl acetate, or chloroform, more sparingly so in water, benzene, or ether, and very sparingly so in light petroleum

II. 2-Acetylaminoveratric acid (2 grams) was mixed with chloroform (4 c.c.) and treated with bromine (1·3 grams) dissolved in chloroform (2 c.c.); the bromo-amide gradually separated, and, after remaining for twenty-four hours, the mixture was treated with water, the chloroform separated, washed with a little dilute alkali, dried, and evaporated, when a small quantity of a neutral substance remained. This was crystallised from a little dilute methyl alcohol, when it crystallised in octahedra melting at 151°, and was found to be 4- or 5-bromo-3-acetylaminoveratrole.

The alkaline washings yielded on acidification 5-bromo-2-acetyl-aminoveratric acid.

5-*Bromo-2-aminoveratric acid* was obtained when the acetyl derivative was hydrolysed with either hydrochloric acid or concentrated sulphuric acid. It crystallises from alcohol in colourless prisms melting at 158—159°:

0·1114 gave 5·6 c.c. N_2 at 31° and 758 mm. N=5·4.
$C_9H_{10}O_4NBr$ requires N=5·1 per cent.

The constitution of this amino-acid was readily proved by the elimination of the amino-group, when 5-bromoveratric acid melting at 191° was obtained (Found: Br=30·5. Calc.: Br=30·6 per cent.).

Bromination of 5-Acetylaminoveratric Acid (XII). 2-*Bromo-5-acetylaminoveratric Acid* (XIII).

The acid (2 grams) was dissolved in acetic acid (4 c.c.) and treated with the calculated quantity of bromine dissolved in a little acetic acid. The clear solution rapidly became cloudy, and a voluminous precipitate of the reddish-yellow bromo-amide separated. After remaining for ten minutes, water was carefully added, when a clear solution was obtained, from which the bromo-acd slowly crystallised. This was collected and recrystallised from dilute alcohol, from which it separated in fine needles:

0·1862 gave 0·1096 AgBr. Br=25·1.
$C_{11}H_{12}O_5NBr$ requires Br=25·1 per cent.

2-Bromo-5-acetylaminoveratric acid melts at 221°. It is readily soluble in hot alcohol or acetone, more sparingly so in the cold solvents; in water or benzene it is sparingly soluble.

On hydrolysis of the acetylamino-acid with hydrochloric acid (50 per cent.), the *amino*-acid was obtained as a viscid oil which rapidly crystallised. It was recrystallised from dilute alcohol, from which it separated in glistening prisms melting at 183°. It is readily soluble in hot alcohol or acetone, but only sparingly so in water, chloroform, or benzene:

0·151 gave 0·1021 AgBr. Br=28·8.
$C_9H_{10}O_4NBr$ requires Br=28·9 per cent.

When diazotised in alcoholic solution with amyl nitrite, it yielded 2-bromoveratric acid, which after crystallisation from methyl alcohol melted at 201—202° (Found: Br=30·2. Calc.: Br=30·6 per cent.).

Bromination of 6-Acetylaminoveratric Acid (XIV). *5-Bromo-4-acetylaminoveratrole* (IX).

The finely divided acid (2 grams) was suspended in chloroform and the calculated quantity of bromine dissolved in chloroform gradually added. The bromine was rapidly absorbed, and simultaneously a small amount of gas (carbon dioxide) was evolved. After remaining overnight, water was added to the pasty mass, when a vigorous evolution of gas was observed. A small quantity of unchanged acid was removed by filtration, the chloroform separated, washed with a little dilute alkali, dried, and evaporated. The deep brown residue rapidly solidified to a hard, crystalline cake, and was purified by crystallisation from hot water, from which it separated in slender, colourless needles melting at 127—128°, and was identical in every way with the compound obtained by the bromination of 4-acetylaminoveratrole. No trace of any other product could be isolated:

0·1144 gave 0·0775 AgBr. Br = 28·9.

$C_{10}H_{12}O_3NBr$ requires Br = 29·2 per cent.

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[*Received, May* 16, 1918.]

LXIX.—*The Electrical Conductivity of Acids and Bases in Aqueous Solutions.*

By JNANENDRA CHANDRA GHOSH.

IN previous papers (this vol., pp. 449, 627, 707), it has been shown that the variation of equivalent conductivity with dilution, in the case of all binary univalent salts, is represented by the equation

$$\frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is Avogadro's number, E the absolute charge on an ion, D the dielectric constant of the solvent, and V the dilution.

Abnormally High Values of Activity-coefficients of Acids and Bases.—Aqueous solutions of strong acids like hydrochloric or nitric acids, and of strong bases like sodium or potassium hydroxides, however, prove exceptions to the above rule. This irregular behaviour will be at once evident from table I, where the values of the activity-coefficients calculated from equation (1) are com-

pared with the observed values (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 474).

TABLE I.

	$V=$ 10.	20.	50.	100.	200.	500.
$\frac{\mu_v}{\mu_\infty}$ calc.	0·844	0·875	0·906	0·924	0·940	0·955
$\frac{\mu_v}{\mu_\infty}$ obs. for HCl.......	0·925	0·944	0·962	0·972	0·981	0·988
$\frac{\mu_v}{\mu_\infty}$ obs. for KOH ...	0·887	0·910	0·933	0·945	—	0·970

This irregularity disappears as we pass from the aqueous to non-aqueous solutions of strong acids. In alcoholic solutions, for example, equation (1) is exactly followed. In table II, the observed values of the molecular conductivity of hydrochloric acid in methyl alcohol are taken from the work of Goldschmidt and Thuesen (*Zeitsch. physikal. Chem.*, 1912, **81**, 32). For dilute solutions, the agreement between observed and calculated values is always within 1 per cent., and the validity of equation (1) is therefore proved beyond doubt.

TABLE II. $T=25°$.

	$V=$	40.	80.	160.	320.	640.
μ_∞ calc. from $\mu_{80}=$ 192·2	μ_v calc.	142·5	151·8	159·5	166·7	170·9
μ_∞ obtained by extrapolation $=192·1$	μ_v obs.	141·0	151·8	160·5	167·2	171·9

Abnormally High Values of the Electrical Conductivity of Acids and Bases.—It has always appeared remarkable that the values of the equivalent conductivity of acids and bases in aqueous solutions are not of the same order of magnitude as those of other salts. Thus the conductivities of hydrogen and hydroxyl ions in aqueous solutions are 318 and 175 respectively at 18°, whilst those of the other ions never exceed 70. In non-aqueous solutions, again, this abnormality is not observed. Thus in ethyl alcohol, the conductivities of hydrogen and hydroxyl ions are 32·1 and 16·5, whilst those of potassium and ammonium ions are 21·5 and 20 respectively (Godlewski, *Zeitsch. physikal. Chem.*, 1905, **51**, 751; Hägglund, *Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 11). Here the values are of the same order. This is also true for solutions in other solvents, for example, methyl alcohol or acetone.

The Conductivity of Aqueous Solutions of Acids and Bases—not entirely a Convection Process.—It is thus evident that the abnormal conductivities of hydrogen and hydroxyl ions, in aqueous solutions,

are somehow related to the high values of the activity-coefficients of acids and bases, both these abnormalities disappearing when the solvent medium is other than water. Equation (1) has a good theoretical basis, and it appears more reasonable to assume that the observed ratio $\frac{\mu_v}{\mu_\infty}$ for acids and bases in aqueous solutions is not a real expression for the activity-coefficient, than to impugn its validity. It appears to the author that the observed conductivity of hydrogen and hydroxyl ions in water is the additive effect of two separate and independent processes, namely, (1) the transference of electricity by the convection of charged bodies, and (2) the transference of electric charge through molecules of water by the alternate processes of dissociation and recombination during impact with hydrogen or hydroxyl ion.

The first process is, of course, the ordinary method of electrolytic conduction met with in salt solutions. Here, only the free ions take part in the transference of electricity, and their number is given by the equation

$$N' = 2N \,.\, e^{-\frac{A}{2RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The mechanism of transport of electricity through molecules of water may be conceived as follows.

A molecule of water is capable of dissociating into hydrogen and hydroxyl ions, the only ions that possess abnormal conductivity. Now, in a dilute solution of hydrochloric acid the hydrogen ion is surrounded by water molecules on all sides. It appears probable that when a hydrogen ion strikes against a molecule of water, the latter in some cases undergoes dissociation. The hydrogen ion thus produced carries away the electric charge by convection, whilst the hydroxyl ion of the water molecule combines with the impinging hydrogen ion to generate a molecule of water. The conception of the process is similar to that imagined by Grotthuss to explain the phenomenon of electrolytic conduction. It may well be that the hydrogen atom of the water molecule, which is farthest from the point of impact, shoots off as a charged particle, and if the process of dissociation and recombination is instantaneous, the electric charge $(+E)$ appears to be carried instantaneously through a distance proportional to the diameter S of the water molecule. Thus at each impact attended with dissociation a distance K_1S is saved, where K_1 is always a fractional quantity. The result is that the hydrogen ion appears to move with a velocity much greater than its true characteristic velocity. Now let $U_{H^\cdot}$ be the real velocity of the hydrogen ion. The total number of impacts with water molecules per second is $K_2N \,.\, \pi \,.\, S_1^2U_{H^\cdot} \,.\, n$, where n is the

number of water molecules in a c.c. and S_1 the diameter of the hydrogen ion. The number of impacts attended with dissociation is $K_3 . K_2 . N . \pi . S_1^2 U_{H^\cdot} . n$, and the distance saved per second $= K_1 . S . K_3 . K_2 . N . \pi . S_1^2 . U_{H^\cdot} . n = C$ at a constant temperature, since K_1, K_2, K_3, $U_{H^\cdot}$, have always the same value at constant temperature. C also does not vary with dilution if n and N do not vary. Now in the case of dilute solutions, the number of solvent molecules in a c.c. may always be regarded as constant, independent of concentration, without introducing much error. Since, according to the theory developed before, strong electrolytes are completely dissociated in dilute solutions, the number of hydrogen ions in a solution containing a gram-molecule is always constant. Whilst in the first process—the transference of electric charge by convection—only the free hydrogen ions take part, this is not the case in the second process. Here it stands more to reason to assume that all the hydrogen ions are equally efficient, for, considering that some of the hydrogen ions are stationary, there is nothing to prevent their collision with water molecules, for the latter are always free to move. In fact, the inactive hydrogen ions are always capable of vibratory motion. The distance C saved per second is thus independent of dilution.

Hence, for solutions of hydrochloric acid, on the basis that the activity-coefficient α at any dilution is the same as that of univalent binary salts, we get

$$\mu_v = \alpha(U_{H^\cdot} + U_{Cl'}) + C_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where α is the activity-coefficient at dilution v, and C_1 a constant independent of dilution. α can always be calculated from equation (1).

Again,

$$\mu_\infty = U_{H^\cdot} + U_{Cl} + C_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From equations (3) and (4),

$$U_{H^\cdot} = \frac{\mu_\infty - \mu_v - (1-\alpha)U_{Cl'}}{1-\alpha} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$C_1 = \mu_\infty - U_{H^\cdot} - U_{Cl'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$U_{H^\cdot}$, the real ionic mobility of the hydrogen ion, and C_1, the conductivity due to the second process, can thus at once be calculated from available data.

Experimental Confirmation of the above Hypothesis.—The experimental data on the conductivity of acids must always yield the same value of C_1 and $U_{H^\cdot}$ provided the acid is a strong electrolyte. This expectation has been fully realised. Thus, for a solution of

hydrochloric acid at dilution 10 and temperature 25°, $\mu_v = 390{\cdot}4$, $\mu_\infty = 426$, $U_{Cl'} = 75{\cdot}8$, and $\alpha = 0{\cdot}844$, whence $U_{H\cdot} = 152{\cdot}4$ and $C_1 = 197{\cdot}8$.

Again, for solutions of nitric acid, at dilution 10, the available data give for $U_{H\cdot}$ 151·3 and 198·8 for C_1 (Noyes and Falk, *loc. cit.*). The values of $U_{H\cdot}$ and C_1 obtained from the data on the conductivity of hydrochloric and nitric acids therefore agree within 1 per cent. We may take 152 as the mean value of $U_{H\cdot}$ and 198·5 as that of C_1. The real mobility of hydrogen ion is therefore of the same order of magnitude as those of the other ions. The second process is thus responsible for the transference of about half the electric current in acid solutions.

The values of $U_{H\cdot}$ and C_1 having once been determined, it is possible to calculate the molecular conductivity of any strong acid at any dilution from equation (3). Tables III and IV show how the calculated values agree with the observed ones.

In table III, the observed values are taken from the work of Noyes and Falk (*loc. cit.*), whilst the data in table IV are obtained from a paper by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 436).

TABLE III.

	$V=$	20.	100.	500.	1000.	2000.
HCl	μ_v calc.	397·6	408·9	416·5	418·4	—
	μ_v obs.	398·4	410·5	418·5	420·4	—
HNO_3	μ_v calc.	393·1	404·5	411·0	—	415·0
	μ_v obs.	393·3	406·0	413·0	—	417·0

TABLE IV.

	$V=$	100.	400.	111.	1600.
Naphthalene-β-sulphonic acid	μ_v calc.	637·2	372·4	375·3	376·3
	μ_v obs.	367·4	374·9	376·9	377·4
Toluene-*p*-sulphonic acid	μ_v calc.	369·9	375·0	377·6	378·5
	μ_v obs.	368·4	375·3	378·2	379·0

The agreement between the observed and calculated values is always within 0·5 per cent.

The real values of $U_{OH'}$ and C_1 for bases can also be obtained in the same way. Thus, at dilution 10, μ_v for potassium hydroxide is 213; μ_∞ is 240·2. From these data, the value of $U_{OH'}$ is 109 and of C_1 for bases 66. Table V shows how exactly the observed values of the molecular conductivity of potassium hydroxide agree with those calculated from equation (3).

TABLE V.

		$V=$	20.	50	100.	500.
KOH	μ_v calc.		218·4	224·0	227·1	232·5
	μ_v obs.		219·0	225·0	228·0	233·0

Arrhenius has already suggested "that the exceptionally great conductivity of these ions ($H^{\cdot}$ and OH') in water is probably due only to the fact that they are the two ions into which water is electrolytically decomposed" ("Theories of Solution," p. 138). In the foregoing pages, an attempt has been made to develop a quantitative explanation of the abnormal mobility of hydrogen and hydroxyl ions by assuming that an electric charge can be transferred almost instantaneously through water molecules during impact with these ions by the converse processes of dissociation and recombination taking place alternately.

A General Hypothesis for all Electrolytes.—The electrolytes can be classified into three groups, namely, (1) consisting of strong electrolytes, (2) containing acids of intermediate strength, "transition electrolytes," and (3) consisting of weak acids and bases where Ostwald's dilution law holds good.

For the first group we have the following empirical laws:

$\mu_v = \mu_\infty - a\sqrt[3]{C}$ (Kohlrausch, *Ann. Phys. Chem.*, 1885, [iii], **26**, 161) . . . . (7)

and

$i = 2 - b - \sqrt[3]{C}$ (Noyes and Falk, *J. Amer. Chem. Soc.*, 1910, **32**, 101) . . . . (8)

Equation (1) becomes identical with Kohlrausch's empirical law in the case of dilute solutions where μ_v is only slightly less than μ_∞. Thus, equation (1) may be put in the form

$$\frac{K}{\sqrt[3]{V}} = \log_e \frac{\mu_\infty}{\mu_v}$$

or

$$K\sqrt[3]{C} = \frac{\mu_\infty - \mu_v}{\mu_\infty} = 1 - \frac{\mu_v}{\mu_\infty} \quad . \; . \; . \; . \; . \quad (9)$$

or

$$\mu_v = \mu_\infty (1 - K . \sqrt[3]{C}) = \mu_\infty - a\sqrt[3]{C},$$

Again, the activity-coefficient

$$a = \frac{\mu_v}{\mu_\infty} = 1 - K\sqrt{C} \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

Noyes and Falk's empirical law can easily be derived by apply-

ing Clausius's virial theorem to salt solutions. It has already been shown that

$$\begin{aligned} i &= n\left\{1 - \tfrac{1}{3}\log_e\frac{\mu_\infty}{\mu_v}\right\} \quad . \quad . \quad . \quad . \quad . \quad (11) \\ &= n\{1 - \tfrac{1}{3}K\sqrt{C}\} \\ &= n - \tfrac{1}{3}n.K.\sqrt[3]{C} \\ &= 2 - b\sqrt[3]{C}, \text{ for binary salts where } n = 2. \end{aligned}$$

Whilst the strong electrolytes of group 1 belong to the limiting case, we have, for the other two groups, as in Arrhenius's original theory, both undissociated molecules and ions in solution. The law of mass action in its original form is, however, not applicable to electrically charged bodies. It requires modification in the sense that only the free ions take part in the equilibrium. It is only the fraction of the total number of ions which, by virtue of their kinetic energy, can overcome the force of electrostatic attraction, that really matter. They only are free to move, and hence have the chance of colliding with one another. From the kinetic point of view, therefore, only these free ions are to be taken into consideration in applying the law of mass action to the process of electrolytic dissociation. Thus, if x is the fraction of a gram-molecule of acid, which has undergone dissociation into ions, the law of mass action is not expressed by the equation

$$\frac{x^2}{(1-x)V} = K,$$

but by the equation

$$\frac{(ax)^2}{(1-x)V} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where a is the activity-coefficient at the ionic concentration $\frac{x}{V}$. Now, a for any dilution can be calculated from equation (1) or (10). In the case of weak acids belonging to the third group, X is generally very small, $\frac{x}{V}$ becomes always negligibly small, and hence a is very nearly equal to one at all dilutions. For very weak acids, therefore, equation (12) becomes identical with Ostwald's dilution law.

A Dilution Formula for Transition Electrolytes.—Here the activity-coefficient a is not always equal to one, and the equation

$$\frac{(ax)^2}{(1-x)V} = K,$$

must be applied as such. According to the ideas developed before,

the equivalent conductivity of an acid of intermediate strength may be equated thus:

$$\mu_v = x \,.\, 198{\cdot}5 + \alpha x(U_{H\cdot} + U_{Anion}) \quad . \quad . \quad . \quad . \quad (13)$$

where x is the gram-equivalent of total hydrogen ion and $U_{H\cdot} = 152$ at 25°, or

$$\mu_v = x \,.\, 198{\cdot}5 + (1 - K\sqrt[3]{C})x \,.\, (U_{H\cdot} + U_{Anion}) \text{ from equation (10)}$$

$$= x(198{\cdot}5 + U_{H\cdot} + U_{Anion}) - K\left(\frac{x}{V}\right)^{\frac{1}{3}} . \, x \,.\, (U_{H\cdot} + U_{Anion})$$

$$\text{or since } c = \frac{x}{V}$$

$$= x \,.\, \mu_{\infty} - \frac{K}{\sqrt[3]{V}} . \, x^{\frac{4}{3}} \,.\, (U_{H\cdot} + U_{Anion}).$$

The equation contains only one unknown quantity, x, and hence it admits of a solution. The real value of x can, however, be easily obtained with great accuracy by the method of successive approximation. x having thus been determined, it is easy to calculate α at concentration $\frac{x}{V}$. Hence all the factors for verifying the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K,$$

can be had from the conductivity data. In tables VI, VII, VIII, and IX four acids have been chosen in the order of increasing strength to illustrate the validity of the above equation. The values of molecular conductivity have been taken from the very accurate work of Kendall (*loc. cit.*). According to this author, M for the hydrogen ion at 25° is 347, whilst the value obtained by Noyes and Falk as the mean of the data given by various workers is 350. In the following tables, the latter value has been accepted as true.

TABLE VI.

Cyanoacetic Acid. $\mu_{\infty} = 389{\cdot}1$ at 25°.

V.	μ_v.	x.	α.	K.
16·82	88·0	0·2370	0·9158	0·00365
33·64	117·0	0·3120	0·9260	0·00361
67·28	152·5	0·4050	0·9352	0·00358
134·56	193·9	0·5125	0·9442	0·00357
269·10	238·7	0·6283	0·9524	0·00358
538·20	282·6	0·7409	0·9606	0·00363
1076·40	320·0	0·8361	0·9673	0·00368

TABLE VII.

o-Nitrobenzoic Acid. $\mu_{\infty} = 382{\cdot}2$ at 25°.

$V.$	$\mu_v.$	$x.$	$\alpha.$	$K.$
32·0	139·7	0·3810	0·9204	0·00621
64·0	179·0	0·4854	0·9310	0·00620
128·0	221·9	0·5984	0·9407	0·00617
256·0	265·0	0·7106	0·9497	0·00616
512·0	303·6	0·8108	0·9588	0·00622
1024·0	333·5	0·8861	0·9664	0·00627

TABLE VIII.

Dichloroacetic Acid. $\mu_{\infty} = 388{\cdot}6$ at 25°.

$V.$	$\mu_v.$	$x.$	$\alpha.$	$K.$
16·0	231·4	0·6337	0·8835	0·0535
32·0	273·2	0·7400	0·9009	0·0534
64·0	309·8	0·8318	0·9174	0·0540
128·0	338·7	0·9020	0·9319	0·0550

TABLE IX.

Trichlorobutyric Acid. $\mu_{\infty} = 379{\cdot}0$ at 25°.

$V.$	$\mu_v.$	$x.$	$\alpha.$	$K.$
23·6	308·8	0·8616	0·8861	0·1783
47·2	331·7	0·9149	0·9068	0·1720
77·26	343·9	0·9434	0·9195	0·1720
108·0	350·4	0·9566	0·9273	0·1800

A comparison of the numbers in column five at once shows that for each acid a constant value of K is obtained. The degree of dissociation in the case of cyanoacetic acid has been varied from 0·23 to 0·83, but the equation holds good exactly throughout this interval.

The applicability of the formula has also been demonstrated for the entire range of transition electrolytes, beginning with cyanoacetic acid, which borders on the type of electrolytes included in the third group, and ending with trichlorobutyric acid, the strength of which is comparable with that of mineral acids.

Summary.

The abnormally high mobility of the hydrogen and hydroxyl ions in aqueous solutions has been explained on the assumption that electricity is partly carried by the ordinary process of convection and partly propagated through water molecules undergoing alternate dissociation and recombination. The apparently high activity-coefficients of strong acids and bases in aqueous solutions

has also been traced to this cause. A modified Ostwald equation, $\frac{(ax)^2}{(1-x)V} = K$, based on the consideration that only free ions have the capacity of regenerating undissociated molecules, has been developed for weaker electrolytes, where the degree of dissociation is less than one. It has been shown that this equation becomes identical with Ostwald's dilution law in the case of very weak electrolytes where a is always very nearly equal to one, and also gives very concordant values for the equilibrium constant in the case of "transition electrolytes" where Ostwald's equation is not applicable.

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LXX.—*The Freezing Point Curve of Mixtures of Toluene*-o- *and* -p-*sulphonamides. Composition of Mixtures of Toluene*-o- *and* -p-*sulphonic Acids.*

By PHYLLIS VIOLET MCKIE.

AN accurate method of estimating the relative amounts of toluene-*o*- and -*p*-sulphonic acids in a mixture of the two acids can be based on the fusion curve of mixtures of the corresponding amides.

The composition of these acid mixtures has previously been investigated by Holleman (*Ber.*, 1911, **44**, 2504), by determining the freezing points of mixtures of the sulphonyl chlorides prepared from them. In this case, toluene-*m*-sulphonic acid was also generally present in small proportion. The freezing points of the *o*- and *p*-chlorides lie on a simple but rather flat eutectic curve. The eutectic point is not well defined, nor has it been directly determined by Holleman. From his figures, it would appear that this point lies in the neighbourhood of 1°, and that the eutectic mixture contains from 15 to 25 per cent. of the *p*-chloride.

The low range of temperature over which many of the mixtures of the *o*- and *p*-chlorides solidify (the *p*-chloride melts at 66·7° and the *o*-chloride at 10·0°, Holleman, *loc. cit.*), and the considerable manipulative difficulties encountered in preparing the mixture of chlorides in a state in which the fusion point can be observed (*loc. cit.*), constitute objections to the use of this method for the purpose

of determining the composition of mixtures of the toluene-*o*- and -*p*-sulphonic acids.

These difficulties are lessened or disappear if the mixture of crude acid chlorides is converted into amides, a transformation which can be very simply and quantitatively carried out. Moreover, it is necessary only to dry the amide mixture before determining the fusion point, whereas the mixture of acid chlorides must finally be distilled under diminished pressure. The melting points of the mixtures of amides lie in a very convenient range of temperature, namely, 110—156°, and, as will be seen from the curve, the eutectic point is extremely sharply defined. The eutectic mixture contains 61·25 per cent. of the *p*-sulphonamide, and melts at 110·25°.

Preparation of Materials.—The toluenesulphonic acid, or mixture of acids, is converted into the sulphonyl chloride by treatment with phosphorus pentachloride and phosphoryl chloride (Polak, *Rec. trav. chim.*, 1910, **29**, 416; compare Holleman, *loc. cit.*), and the sulphonyl chlorides are extracted with ether from the product of the reaction after it has been treated with ice. After some of the ether has been evaporated, solid ammonium carbonate, and finally some alcoholic ammonia, is added, the mixture being gently warmed by placing it at intervals on a water-bath. The reaction is known to be complete when the very penetrating odour of the sulphonyl chloride has disappeared. The conversion may also be conveniently effected by grinding the mixture in a mortar.

The product of amidation, after the evaporation of solvents, is extracted with as little cold water as possible to remove ammonium salts, and then dried at 100° to expel the water of crystallisation of the *p*-amide.

The *p*-amide separates from aqueous solution with two molecules of water. The dihydrate melts, if heated rapidly, at 105°, but is best rendered anhydrous by drying at 100°:

0·1730 when dried at 100—110° for two hours lost 0·0282. $H_2O=16·3$.

$C_7H_9O_2NS,2H_2O$ requires $H_2O=17·3$ per cent.

Both the *o*- and *p*-amides can be purified and almost completely freed from the isomeride by careful crystallisation from water. Final purification was effected by sublimation in the vacuum of a Töpler pump, which raised the melting point by a few tenths of a degree. Resublimation of material which had been thus treated produced no further change.

The melting point of toluene-*p*-sulphonamide is given as 137° (Klason and Vallin, *Ber.*, 1873, **12**, 1853), and that of toluene-*o*-

sulphonamide as 153—154° (Wolkow, *Zeitsch. für Chem.*, 1870, 327) and 155° (Noyes, *Amer. Chem. J.*, 1886, 8, 176). After sublimation in a vacuum, the latter melts at 156·3° and the former at 137·45°.

Determination of the Fusion Points.—Holleman recommends a special form of heating-bath (*loc. cit.*), by means of which stirring is avoided. In the present work, the following arrangement was employed: The heating-bath is a beaker containing clear, colourless glycerol, and is fitted with a stirrer. The material is placed in a small tube, fitted with a thermometer reading to 0·1° and a stirrer. This tube is enclosed in a larger tube, so that an air-space prevents direct contact with the glycerol. Sufficient material is taken to ensure that the bulb of the thermometer is completely covered by the molten mass. With the thermometer and the tube which were used, 0·5—1·5 grams were required. The whole apparatus was carefully screened from draughts.

The heat was supplied by a small hooded gas-jet, regulated by a screw clip compressing the rubber tubing. No difficulty was experienced in keeping the temperature of the bath constant over considerable periods. When determining a melting point, the temperature of the bath was raised to within a degree or so of the expected fusion point *before* introducing the jacketed tube containing the material. Prolonged heating and sublimation were thus avoided. The inner tube with its fittings—thermometer and stirrer—and containing the material, was weighed before and after a determination in order to check any loss through sublimation. The maximum loss observed in any case amounted only to 0·0004 gram on a total weight—tube, thermometer, material, etc.—of 10 grams.

The temperature of the bath is gradually raised until incipient fusion is observed. At no time was the temperature of the heating-bath more than 1° above that registered by the thermometer in the material. The melting point is taken as the temperature at which the material liquefies, save for one or two crystals. On maintaining the thermometer steady for ten to fifteen minutes, the crystals should not disappear. On raising the temperature 0·1°, they should melt.

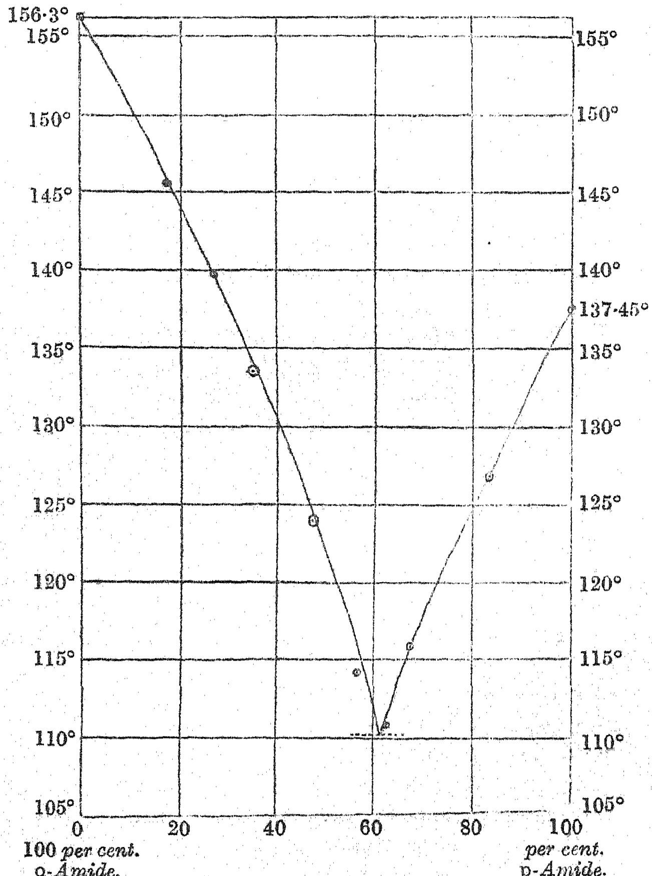
In the case of the pure substances, the variation of the thermometer from the point of incipient fusion to complete melting did not extend to more than 0·5°.

Toluene-p-*sulphonamide.*—Middle fraction of the sublimate obtained by sublimation in vacuum.

(1) Incipient fusion, 137°; bath, 138° for ten minutes. All but

one crystal melted, 137·40°; bath, 138° for fourteen minutes. Last crystal melted, 137·5°.

(2) The temperature was kept at 137·45° for five minutes; all but one crystal melted. This melted on raising the temperature to 137·5°, bath 138°. The melting point of toluene-*p*-sulphonamide is therefore taken as 137·45°.



Toluene-o-sulphonamide.—The crude material has an average melting point of 148—152°. One recrystallisation from water raises the melting point to 154—155°. On further recrystallisation, the melting point is raised to 156°. Material which had been recrystallised from water was sublimed in a vacuum. As in the former case, all but the middle fraction was neglected.

(1) Incipient fusion, 156·1°; bath, 157° for ten minutes. All

but one crystal melted, 156·3°; bath, 157° for ten minutes. Last crystal melted, 156·4°.

(2) The external temperature was maintained at 156·7° for twenty minutes, the temperature of the inner thermometer registering 156·3°. A trace of solid remained, which melted on raising the temperature to 156·4°. The melting point of toluene-*o*-sulphonamide is therefore taken as 156·3°.

Plotting of the Curve.—The melting point of a weighed portion of one of the components was determined. Successive weighed portions of the other pure component were then added, and the melting point was determined for each mixture. The curve was followed, starting from both the pure ortho- and the pure para-compound. When the curve had been plotted in this way, single points on it were determined, separate mixtures being made up for each determination.

o-Amide. Gram.	*p*-Amide. Gram.	*p*-Amide. Per cent.	Melting point.
0·3241	0	0	156·3°
0·3241	0·0709	17·96	145·5
0·3958	0·1381	25·87	139·7
0·3235	0·1787	35·58	133·6
0·3958	0·2698	40·54	130·3
0·3235	0·2839	46·74	124·0
0·3958	0·4020	50·39	120·8
0·2478	0·3267	56·87	114·1
0·3958	0·6230	61·15	110·4
0·3958	0·8200	67·45	115·9
0·1212	0·5752	82·59	126·8
0·2839	0·0	100·0	137·45

I wish to express my thanks to Professor Orton, at whose suggestion and under whose direction this work has been carried out, for his guidance and criticism.

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LXXI.—*The Compound* $H_2B_4O_6$ *and its Salts.*

By RAMES CHANDRA RAY.

IN a previous communication (T., 1914, **105**, 2162), it was shown that the so-called amorphous boron, prepared by the reduction of boron trioxide by means of magnesium, probably consisted of a solid solution of a lower oxide of boron, sometimes in combination with a little magnesium oxide, in elementary boron. If this were

really the case, it appeared probable that the soluble part of the fusion would contain some of the lower oxide, together with excess of boron trioxide, and the present investigation was undertaken with a view to detect and isolate the lower oxide.

The fusion obtained by heating a mixture of boron trioxide with magnesium powder generally contains magnesium boride, amorphous boron (so-called), magnesium oxide, partly in combination with boron trioxide, and, as will be shown later, the lower oxide or oxides of boron. If the operation is carried out under conditions which will now be described, the quantity of magnesium boride in the mixture is very small, although it cannot be altogether eliminated.

A mixture of 1 part of magnesium powder and 3·5 parts of anhydrous boron trioxide, finely powdered and passed through a 120-mesh sieve, was heated in a covered magnesia-lined crubible, through which a current of hydrogen was passed, to a bright red heat for about three hours. After cooling in an atmosphere of hydrogen, the mass was powdered and mixed with half its weight of anhydrous boron trioxide. The mixture was then heated again as before. The fused mass was powdered, water was added to it, and it was allowed to remain for from one to three days, to allow of the decomposition of traces of magnesium boride.

The solution was filtered, and the boric acid removed by the method employed by Travers, Ray, and Gupta (*Pamphlet*, H. K. Lewis and Co., 1916), which consisted in shaking the solution in a vacuum for several days with precipitated magnesium hydroxide, and removing the excess of the latter, together with the insoluble magnesium metaborate, by filtration In analysing the solutions, advantage was also taken of the fact, discovered by Travers, Ray, and Gupta (*loc. cit.*), that when solutions of the lower oxides of boron are evaporated with excess of lime and the residue ignited to constant weight, oxidation does not take place and the increase in the weight of the lime corresponds with the weight of the lower oxide in the solution. For the purpose of analysis, three equal quantities of the solution were treated as follows:

(*a*) The magnesium was precipitated in the usual manner and the result expressed as the oxide MgO.

(*b*) The solution was introduced into a platinum crucible containing lime, ignited to constant weight, and, after evaporation to dryness, the crucible was again ignited to constant weight, the increase in weight giving the weight of the magnesium oxide and of the lower oxide of boron, together with the weight of any trace of boric acid left in the solution.

(c) The third portion of the solution was evaporated to dryness in a vacuum and the residue heated in a sealed bulb with concentrated nitric acid. The bulb became filled with red fumes, and the lower oxide of boron was oxidised to boron trioxide. The bulb was then opened, the excess of nitric acid removed by evaporation in a vacuum desiccator over solid sodium hydroxide, and the boric acid determined by the lime method.

The following are the results of the experiments:

	I.	II.	III.	IV.	V.
MgO per 100 c.c. of solution	0·0980	0·1156	0·1248	0·0876	0·1608
Residue less MgO per 100 c.c.	0·3048	0·3584	0·3896	0·2726	0·5012
B_2O_3 from residue per 100 c.c.	0·3452	0·4036	0·4324	0·3048	0·5664
MgO in gram-mols. per 100 c.c.	0·0024	0·0029	0·0031	0·0022	0·0040
B in gram-atoms per 100 c.c.	0·0099	0·0115	0·0123	0·0087	0·0161
Ratio B/Mg	4·1	3·9	4·1	3·9	4·0
$\frac{B_2O_3}{\text{(Residue less MgO)}}$	1·132	1·126	1·112	1·118	1·130

It is clear that the ratio B/Mg is very near 4, and that the mean value of the ratio B_2O_3/(Residue less MgO), which is 1·124, closely approximates to the value of the ratio $2B_2O_3/B_4O_5$, which is 1·129. The analytical results appear, therefore, to suggest that the solution contains a magnesium borite, the formula of which may be written MgO,B_4O_5. The oxide B_4O_5 has already been described by Travers, Ray, and Gupta (*loc. cit.*).

Each of the solutions used in these experiments was obtained from the treatment of a different fusion, and it was possible, therefore, although hardly probable, that the constancy of their composition might be attributable to the fact that the conditions in each case were similar. The third preparation was therefore treated with water four times, and the extracts were investigated separately. The results of the analysis of the first extract have already been given; those of the remaining extracts are tabulated below:

	III, *a*.	III, *b*.	III, *c*.
MgO per 100 c.c.	0·0960	0·0616	0·0412
Residue less MgO per 100 c.c.	0·2940	0·1804	0·1212
B_2O_3 from residue per 100 c.c.	0·3290	0·1996	0·1368
MgO in gram-mols.	0·0024	0·0015	0·0010
B in gram-atoms	0·0094	0·0057	0·0039
Ration B/Mg	3·9	3·8	3·9
$\frac{B_2O_3}{\text{(Residue less MgO)}}$	1·119	1·106	1·128

Although the solutions became more and more dilute with each treatment of the fusion with water, their composition remained

practically constant, leaving no room for doubt that the compound MgO,B_4O_5 is really present in them.

It has not been found possible to isolate the magnesium borite.

The molecular weight of the compound can be determined with sufficient accuracy from the freezing points of the solutions. If the magnesium salt were completely dissociated, the molecular weight of the corresponding oxide could be determined from the formula

$$\Delta = 18{\cdot}5(W/M + W'/40),$$

where W is the weight, in 100 c.c. of the solution, of the oxide of boron, M its molecular weight, and W' the weight of the magnesium oxide present. Since, however, the compound is probably dissociated only to the extent of about 75 per cent., the result will be about 15 per cent. too high.

For the determination of the freezing points, measured quantities of the solutions, of which the analyses have already been given, were evaporated to dryness in a vacuum. The residues were dissolved in a measured quantity of water, and the freezing points were compared with the freezing point of pure water. The following results were obtained:

	I.	II.	III.	IV.	V.
W	0·3048	0·3584	0·3896	0·2726	0·5012
W'	0·0980	0·1156	0·1248	0·0876	0·1608
Δ	0·090	0·105	0·115	0·082	0·148
M	121	128	125	124	125
Ratio B_4O_5/MgO	1·0	0·95	1·0	1·0	1·0

The values for M agree sufficiently well with the theoretical value, 124, as calculated for the formula B_4O_5.

On addition of ammonia to the solution, the magnesium is almost completely precipitated as hydroxide, and if the ammoniacal solution is evaporated in a vacuum, a residue is left which consists mainly of the oxide. As Travers, Ray, and Gupta have shown (*loc. cit.*), the oxide is very unstable and is readily oxidised to boric acid.

If a solution of the magnesium salt is treated with potassium hydroxide in equivalent proportions, and afterwards evaporated in a vacuum to small bulk, practically the whole of the magnesium separates as hydroxide and can be filtered off. On further concentration of the solution in a vacuum, the potassium salt separates as a crust which can be redissolved, and the salt purified by crystallisation five or six times, and finally dried in a vacuum at 80—90°. The preparation is a difficult one, and altogether only 2 to 3 grams

of the substance were finally obtained. The salt is stable in the absence of moisture.

The potassium was estimated by first dissolving the salt in water, evaporating the solution to dryness in a platinum vessel, and treating the residue repeatedly with hydrochloric acid and methyl alcohol. The potassium chloride was finally converted into sulphate. For the estimation of boric acid, the solution was saturated with carbon dioxide and boiled under a reflux condenser in a current of pure air. The boric acid was titrated with $N/20$-alkali in the presence of mannitol, using phenolphthalein as indicator:

I. 0·5036 gave 0·3987 K_2SO_4 and 0·3142 B_2O_3. K=35·5; B=19·6.

II. 0·2286 gave 0·1821 K_2SO_4 and 0·1433 B_2O_3. K=35·7; B=19·7.

III. 0·3678 gave 0·2889 K_2SO_4 and 0·2318 B_2O_3. K=35·2; B=19·8.

$K_2B_4O_6$ requires K=35·8; B=20·2 per cent.

The analyses are concordant, and the results in agreement with the values corresponding with the formula $K_2B_4O_6$, which may therefore be accepted as correct.

The molecular weight of the substance was determined by the cryoscopic method, using 20 grams of solvent:

0·0435 gave $\Delta^t = -0·052$. M.W.=78.

0·0874 " $\Delta^t - 0·097$. M.W.=84.

The value of the molecular weight calculated for the formula $K_2B_4O_6$ is 218, and if the compound were completely dissociated in solution, the apparent molecular weight would be 73. The concentrations of the two solutions correspond with 1 gram-equivalent in 100 and 50 litres respectively, and if the salt is ionised to the same extent as similar potassium salts, the degree of ionisation in the two solutions will be approximately 0·9 and 0·8. Without going further into the matter, it is obvious that, within the limits of experimental error, the result proves that the substance in solution has the formula $K_2B_4O_6$, and not the formula KB_2O_3, which would dissociate into two ions and give an apparent molecular weight of approximately 50.

The existence of the anhydrous salt, $K_2B_4O_6$, of the acid $H_2B_4O_6$ is of interest, as it goes to confirm the views put forward by Travers, Ray, and Gupta (*loc. cit.*) as to the constitution of the borohydrates containing four atoms of boron. If the boron atoms in these compounds are linked in a single chain, the oxide, B_4O_5,

which can be obtained by heating them, must be given the formula $\underbrace{BO{:}BO\cdot BO{:}BO}_{O}$, and the corresponding acid the formula

$$BO(OH){:}BO\cdot BO{:}BO(OH).$$

The results do not offer any positive evidence that the so-called amorphous boron is a solid solution of the oxide B_4O_5 in elementary boron, particularly as Travers, Ray, and Gupta have found indications of the existence of the oxide B_2O, which is quite insoluble in water, and may be the oxide that is present in the solid solution. The research has, however, led to the discovery of a new series of compounds, the acid, $H_2B_4O_6$, and its salts, and the results serve to extend our knowledge of the more complex compounds of boron.

In conclusion, I desire to thank Dr. M. W. Travers, F.R.S., at whose suggestion the research was undertaken, for the valuable help which I have always received from him.

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LXXII.—*The Hydrates and Alcoholate of Calcium Benzoate.*

By FREDERICK STANBRIDGE.

THE investigations recorded in this paper were suggested by a chance observation by Dr. C. F. Baker of the action of alcohol on calcium benzoate. This salt, in its usual form, is a crystalline trihydrate having the formula $Ca(C_6H_5\cdot CO_2)_2,3H_2O$. When heated on the water-bath, it loses part of its water, and it was noticed that when this partly dehydrated substance was covered with alcohol, a distinct change in appearance took place, the substance becoming flocculent.

Close examination under the microscope of the action of alcohol on the trihydrate showed the presence, a minute after adding the alcohol, of nuclei on each crystal from which, as centres, bundles of new, needle-shaped crystals grew with great rapidity. Similar results were obtained in tests made under the microscope on the completely dehydrated salt, obtained by heating the trihydrate in an air-oven, in which the original crystalline shape was retained in spite of the loss of water.

These observations point to the formation of a compound of calcium benzoate and alcohol, formed from the anhydrous substance by the simple addition of alcohol, and from the trihydrate by the substitution of alcohol for the water of crystallisation. This compound was prepared and analysed.

The calcium benzoate was prepared specially from pure benzoic acid and pure precipitated calcium carbonate by the usual method. The average yield of the trihydrate from 40 grams of benzoic acid was: first crop, 34 grams; second crop, 11 grams; third crop, 4 grams, a total of 49 grams, representing 89 per cent. of the theoretical yield, which is 55·1 grams. The purity of the salt was checked by estimations of the water and of the calcium. (Found: $H_2O=15{\cdot}80$, $15{\cdot}74$; $Ca=14{\cdot}15$, $14{\cdot}12$. Calc.: $H_2O=16{\cdot}08$; $Ca=14{\cdot}21$ per cent.)

The new compound was prepared by first dehydrating 10 grams of the trihydrate in the air-oven at about 150°, allowing to cool, and then adding 30 c.c. of alcohol specially dried by distillation from quicklime. The mixture became warm and set to a soft mass. It was allowed to remain for a day, being stirred a few times to break up lumps. The excess of alcohol was removed by filtration, and the solid product pressed between filter-paper. After drying in the air, analysis showed that the substance had reverted almost completely to the trihydrate. (Found: $H_2O=15{\cdot}99$ per cent.) In order to ensure drying, and yet to prevent the elimination of combined alcohol, it was found satisfactory to place the product over a mixture of anhydrous calcium chloride and alcohol for four days.

The dried material is a light, white powder having a strong odour of alcohol. Under the microscope, it was seen to consist of very small, transparent needles which, on the addition of a drop of water, clotted together in semi-opaque masses, with needle-shaped crystals projecting from their boundaries. On gently heating a small portion of the substance in a test-tube, alcohol was given off copiously, and this condensed to liquid in the upper, cooler part of the tube. With sodium carbonate and iodine solutions the substance gave the iodoform reaction for alcohol.

In order to determine the exact proportions of alcohol and water in combination in the product, the matter volatile up to 150° was estimated by combustion. A sample was weighed in a small U-tube, and then this was half immersed in a beaker of sulphuric acid provided with a thermometer and stirrer. The temperature of the bath was raised to 150°, while a stream of pure and dry air was passed through the U-tube and thence through a combustion tube filled with copper oxide and heated in a furnace. The

water and carbon dioxide were absorbed and weighed as usual, and from the weights of these the quantities of water and alcohol in the sample were calculated. Analyses at intervals gave the following results, after correction by a blank experiment:

Time after placing over calcium chloride and alcohol.	Water, per cent.	Alcohol, per cent.
4 days	0·51	24·36
5 ,,	0·11	24·68
7 ,,	2·03	24·46
17 ,,	—	24·02
494 ,,	2·03	21·61
$Ca(C_6H_5{\cdot}CO_2)_2,2C_2H_6O$ requires	0	24·61

The results leave no doubt that the substance is a dialcoholate of calcium benzoate, having the formula $Ca(C_6H_5{\cdot}CO_2)_2,2C_2H_6O$. Calcium benzoate thus shows a property which is shared by a number of other salts of calcium, of taking up alcohol to form an unstable additive compound.

The next question that presented itself was, What happens when the trihydrate is treated with alcohol? As alcohol is hygroscopic, it should extract water from the trihydrate, but whether a lower hydrate, the anhydrous salt, or the alcoholate is to be expected as the result cannot be stated without further investigation as to the compounds possible and the conditions under which these are stable.

Rough experiments, made by adding different mixtures of alcohol and water to the trihydrate, to ascertain between what limits of composition action took place at the ordinary temperature, showed that a mixture containing 95 per cent. of alcohol by volume had no action, whilst one containing 97 per cent. acted rapidly.

Attempts to determine by a dilatometer the temperature at which a given mixture of alcohol and water just begins to act on the trihydrate met with no success, but using the thermometric method with the same mixture of alcohol and water ($D^{15\cdot6}$ 0·8149, corresponding with 92·85 per cent. of alcohol by weight), a marked change was observed to take place at 35·5°, the trihydrate being transformed into silky, oblong plates. After separating these and drying them over a mixture of calcium chloride and alcohol for one to two days, analyses were carried out in the same way as in the case of the alcoholate:

Found: $H_2O = 6{\cdot}43$, $6{\cdot}42$; $C_2H_6O = 0$.

$Ca(C_6H_5{\cdot}CO_2)_2,H_2O$ requires $H_2O = 6{\cdot}00$ per cent.

The new substance is therefore the monohydrate formed from the trihydrate by the extraction of 2 molecules of water of crystallisation by the mixture of alcohol and water.

Since another hydrate of calcium benzoate besides the ordinary one had thus been found, it was decided to make a study of calcium benzoate by itself to see what possible substances might be formed by the action of alcohol on the trihydrate.

In order to search for transition points, a dilatometer was first used, containing trihydrate and anhydrous substance and filled with amyl alcohol in one set of experiments, and containing trihydrate and monohydrate and filled with toluene in another set. Beyond slight evidence of a transition point below 90° in the second set of experiments, no very definite results were obtained.

The measurement of the solubility of the trihydrate at various temperatures was adopted finally as the best method. The apparatus used was similar to that described by Lumsden (T., 1902, **81**, 350), employing, however, a hot-air motor for stirring the thermostat tank, an electro-motor for stirring the mixture of crystals and water, and a mercury thermo-regulator of the Ostwald pattern. A gas-pressure regulator of the form *A* described by Stansfield (*Trans. Faraday Soc.*, 1911, **7**, 116) was employed, by which the temperature in the thermostat tank could be kept constant within 0·1° quite easily, even at the highest temperature, 97°, at which the tank was used. After placing the solubility apparatus in position in the tank, the mixture of crystals and water was stirred for periods varying from $4\frac{1}{4}$ to $12\frac{1}{4}$ hours. The mixture was then filtered into a receiver while the whole apparatus was still immersed. At first a small flask was used as receiver, and from this about 10 c.c. of the solution were transferred to a weighed platinum crucible for analysis. For determinations at 80° and upwards, the flask was replaced by a weighing bottle, into which the solution was filtered directly in order to obviate, as far as possible, loss of water by evaporation during the transference of the hot solution, and, after weighing, the solution was poured into a platinum basin for analysis. This apparatus and procedure sufficed for temperatures from about 20° up to 97°. For 10°, the temperature of the tank was adjusted by passing a stream of ice-cold water through the zig-zag tube provided for the purpose on the bottom of the tank. For 0°, the same saturation and filtration apparatus was immersed in clean, chopped ice. For determinations at the boiling point of the saturated solution, at first the Beckmann ebullioscopic apparatus was employed. Excess of the powdered crystals was boiled with distilled water in the apparatus for about three hours, and the temperature and barometric height were noted. Some of the solution was then drawn by suction into a weighing bottle through a tube to the lower end of which was attached a small glass bulb filled with cotton wool in order to

retain any solid. The sample was weighed and transferred to a platinum basin for analysis. The boiling point of pure water was determined in the same apparatus under the same conditions, the barometric height being again noted. From the latter observation, the correction to be added to the observed temperature of the boiling solution to get the true temperature was obtained, and from this the elevation of the boiling point of the saturated solution above that of pure water. Later it was found simpler to boil excess of the powdered crystals with water in an ordinary boiling tube with a layer of beads at the bottom and with a small reflux condenser at the top, the barometric height during the course of the experiment being noted. The temperature of the boiling solution was obtained indirectly by adding to the boiling point of pure water at the observed pressure, as given by tables, the mean elevation of the boiling point by saturation with the crystals as determined by the first experiments with the Beckmann apparatus.

In all cases, in order to estimate the strength of the saturated solution, this was evaporated to dryness, the residue repeatedly treated with concentrated sulphuric acid and ignited, and the calcium weighed as calcium sulphate.

When 90° was passed, results were obtained which appeared anomalous, but this was soon found to be due to the existence of a transition point between 80° and 90°. Special care was taken in this interval of temperature, and the solubility was measured at about 83°, 85°, 87°, and 89°, whereby it was ascertained that the transition point is near 85°, and that the solubility curve above this temperature is distinct from that below. It was possible to obtain points on the metastable portions of both curves near 85° which enabled them to be plotted, and therefore the transition point to be ascertained with greater accuracy. The change from the hydrate stable at the lower temperatures to that stable at the higher temperatures is so sluggish at 90° that three of the ordinary solubility determinations, lasting for seven or eight hours, for which the mixture of crystals and water was heated to 90°, but not above, gave points on the curve for lower temperatures. For the same reason, to get the points for 85°, 87°, 89°, 91°, and 93° on the curve for higher temperatures, it was found necessary to heat the mixture to 98° before the period of saturation. To obtain results for 83° on the metastable portion of the curve for higher temperatures, it was found satisfactory to mix calcium benzoate, completely dehydrated, with a hot solution saturated at the boiling point, and to cut down the time of mixing and stirring at 83° to about two hours.

All results which were not obviously untrustworthy are collected

in table I. Each was obtained from a separate complete experiment, unless indicated otherwise by brackets. The temperatures have been corrected, and are probably true to 0·1°. The solubility is expressed as grams of anhydrous calcium benzoate per 100 grams of water. The hydrate that is in contact with the saturated solution is denoted by the figure I for that stable at lower temperatures and II for that stable at higher temperatures.

TABLE I.

Temperature.	Solubility.	Hydrate.	Temperature.	Solubility.	Hydrate.
0·2°	2·235	I	84·9°	7·652	II
0·2	2·229	,,	87·0	7·702	,,
0·2	2·232	,,	87·0	7·705	,,
9·8	2·454	,,	87·0	7·718	,,
9·8	2·452	,,	89·1	7·832	,,
19·9	2·720	,,	89·1	7·870	,,
19·9	2·726	,,	89·1	7·848	,,
19·9	2·722	,,	89·1	7·852	,,
29·8	3·016	,,	90·3	8·614	I metastable
30·1	3·026	,,	90·2	8·529	,, ,,
39·7	3·426	,,	90·2	8·523	,, ,,
39·7	3·421	,,	91·1	8·040	II
39·7	3·426	,,	91·1	7·949	,,
49·7	4·070	,,	91·1	8·026	,,
49·7	4·032	,,	93·2	8·237	,,
49·7	4·056	,,	93·1	8·198	,,
49·7	4·036	,,	93·2	8·087	,,
59·8	4·719	,,	93·1	8·095	,,
59·8	4·699	,,	95·2	8·349	,,
59·8	4·708	,,	95·2	8·371	,,
69·7	5·630	,,	95·2	8·424	,,
69·9	5·618	,,	95·2	8·371	,,
69·7	5·710	,,	97·2	8·450	,,
70·0	5·769	,,	97·2	8·453	,,
70·0	5·650	,,	97·2	8·539	,,
79·6	6·857	,,	97·2	8·513	,,
79·9	6·865	,,	Boiling point 100·2	8·800	,,
82·9	7·561	II metastable	99·6	8·537	,,
82·9	7·502	,, ,,	100·0	8·455	,,
82·9	7·518	,, ,,	99·4	8·610	,,
82·9	7·528	,, ,,	99·5	8·766	,,
84·9	7·614	II	100·6	8·880	,,
85·0	7·563	,,	100·4	8·814	,,

Many efforts were made to obtain specimens of the solid hydrate stable in contact with saturated solution above the transition point. The first method used was that described by Lumsden (*loc. cit.*), the apparatus employed being similar to that figured by him. No results of any value were obtained; the solid product was a fine white powder, and consequently retained a considerable quantity of saturated solution. By the second method, two small quantities of the trihydrate were heated in separate small bulbs in communication with one another to temperatures above the

transition point, but one somewhat higher than the other, whereby the water in the saturated solution formed in the first was made to distil gently over into the second until no further loss of weight of the first bulb and contents could be detected. In two experiments of this kind there was a loss of 30·22 grams and 30·48 grams of water per gram-molecule of the trihydrate in the hotter bulb, suggesting the formation of the monohydrate, for which the loss of weight per gram-molecule of the trihydrate would be 36 grams.

It appeared desirable to complete the study of the equilibrium of solutions of calcium benzoate in water by determining the freezing-point curve of solutions of various strengths. The measurements of the freezing points were carried out in the usual manner with the Beckmann apparatus. The experiments were made in two series, in the first of which successive quantities of powdered trihydrate were added to a given quantity of water in the apparatus, whereas in the second a stock solution of calcium benzoate was made, slightly more concentrated than the solution saturated at 0°, and the freezing points of this and of solutions consisting of 80, 60, 40, and 20 c.c. of the stock solution diluted to 100 c.c. with water, were determined. The results of the two series of experiments are given in table II.

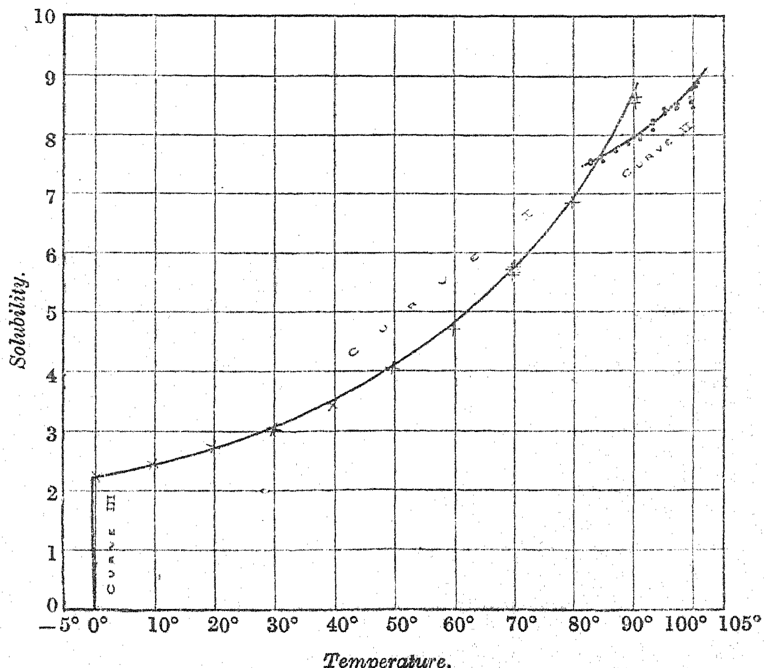
TABLE II.

1st Series.		2nd Series.	
Grams of $Ca(C_6H_5 \cdot CO_2)_2$ per 100 grams of water.	Freezing point.	Grams of $Ca(C_6H_5 \cdot CO_2)_2$ per 100 grams of water.	Freezing point.
0	0°	0	0°
0·3098	−0·100	0·4473	−0·129
0·7680	−0·220	0·8964	−0·159
1·421	−0·308	1·347	−0·282
1·760	−0·370	1·801	−0·289
—	—	2·263	−0·382
—	—	3·470	−0·369

The mean graphs for the two sets of determinations do not coincide very nearly, but by taking points midway between them along the ordinates, it is possible to make, for a given quantity of calcium benzoate in solution, an approximation to the freezing point correct to about 0·01°. The cryohydric point was about −0·37°.

The results in tables I and II are shown in the diagram, which represents completely the stable equilibrium between calcium benzoate and its solutions at all temperatures between the cryohydric point and the boiling point of the saturated solution. The

solubility curve consists of two distinct portions, the one (I) for the lower temperatures defining equilibrium between the trihydrate and saturated solution, the other (II) for the higher temperatures defining that between a lower hydrate and saturated solution. The two curves cross at 84·7°, corresponding with a concentration of 7·62 grams of calcium benzoate per 100 grams of water, and this is therefore the transition point. Curve III is the freezing-point curve, and the concentration at the cryohydric point −0·37°, obtained by extrapolation of curves I and III, is



2·22 grams of calcium benzoate per 100 grams of water. As regards the solid phases, that corresponding with curve I is undoubtedly the trihydrate. Although it has not been possible to isolate from the saturated solution that corresponding with curve II, there is reason for supposing it to be the monohydrate, $Ca(C_6H_5\cdot CO_2)_2,H_2O$.

Summary.

Anhydrous calcium benzoate combines with alcohol to form a dialcoholate, $Ca(C_6H_5\cdot CO_2)_2,2C_2H_6O$, which is very unstable.

Mixtures of alcohol and water containing much alcohol extract

water from the crystalline trihydrate, $Ca(C_6H_5\cdot CO_2)_2,3H_2O$, to form a monohydrate, $Ca(C_6H_5\cdot CO_2)_2,H_2O$.

A study of the solubility of the trihydrate at various temperatures shows that a lower hydrate exists, the transition temperature being 84·7° and the solubility 7·62 grams of calcium benzoate per 100 grams of water. This lower hydrate is probably the monohydrate, $Ca(C_6H_5\cdot CO_2)_2,H_2O$.

A study of the freezing points of solutions of calcium benzoate shows that the cryohydric point is −0·37°, when the solution contains 2·22 grams of calcium benzoate per 100 grams of water.

The action of mixtures of alcohol and water on hydrates should furnish some interesting examples of equilibria in systems of three components with one liquid and two or more solid phases, but the author has refrained from introducing into the present example any theoretical speculations based on the phase rule without further experimental work.

In conclusion, the author desires to record his grateful appreciation of the sympathetic interest taken by Dr. C. F. Baker in the course of the work.

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LXXIII.—N-*Acyl Derivatives of Carbazole.*

By MAURICE COPISAROW.

IN the course of certain investigations, it was found necessary to prepare *N*(9)-acyl derivatives of carbazole.

As but few substances of this class are known,* it was decided to investigate this subject further, this being the more desirable, as the known methods of preparation are not satisfactory.

The drawbacks of the methods so far employed are: (1) The necessity of heating the acid chloride or anhydride with carbazole

* *N*-Acetylcarbazole (Graebe and Glaser, *Annalen*, 1872, **163**, 351; Böeseken, *Rec. trav. chim.*, 1912, **31**, 164), carbazole-*N*-carboxylic acid (Ciamician and Silber, *Gazzetta*, 1882, **12**, 272; Oddo, *ibid.*, 1911, **41**, I., 255), *N*-benzoylcarbazole (Bizzarri, *ibid.*, 1890, **20**, 413; Mazzara, *Ber.*, 1891, **24**, 279), and carbazole-*N*-carbonyl-*o*-benzoic acid (Stümmer, *Monatsh.*, 1907, **28**, 411).

to a comparatively high temperature before the reaction takes place, the product being impure and the yield low; (2) the employment of condensing agents, such as sulphuric acid, ferric chloride (Böeseken, *loc. cit.*), and aluminium chloride (Stümmer, *loc. cit.*; Scholl and Neovius, *Ber.*, 1911, **44**, 1249), which may cause the formation of *C*-acyl derivatives of carbazole (Borsche and Feise, *Ber.*, 1907, **40**, 378); and (3) the constitution of the carbazole derivatives so formed is established only in an indirect or negative manner.

The author has found that by adopting in this case a method analogous to that generally employed in the preparation of *N*-alkyl derivatives of carbazole, namely, condensing the acid haloids, usually the chlorides, with potassium carbazole, good results are obtained.

The general mechanism of formation of the *N*-acyl derivatives of carbazole can be represented by the following equations:

$$C_{12}H_8NK + R\cdot COCl = \underset{\text{(I.)}}{C_{12}H_8N\cdot COR} + KCl, \text{ and}$$

$$2C_{12}H_8NK + R{<}^{COCl}_{COCl} = \underset{\text{(II.)}}{C_{12}H_8N\cdot CO\cdot R\cdot CO\cdot NH_8C_{12}} + 2KCl.$$

It was observed that the energy of reaction and the stability of the products decrease with the complexity of the acyl group in the case of monobasic acids.

It has also been noted that in the case of the *C*- and *N*-acyl derivatives of carbazole, their solubility and fusibility diminish with the increase in the number of carbazole groups in the molecular structure of the product (Stümmer, *loc. cit.*; Scholl and Neovius, *loc. cit.*; Ehrenreich, *Monatsh.*, 1911, **32**, 1102; Copisarow and Weizmann, T., 1915, **107**, 878).

The *N*-acyl derivatives of carbazole investigated by the author give colourless solutions in concentrated sulphuric acid, these solutions assuming a deep green coloration on the addition of a few drops of concentrated nitric acid, the only exception being *N*-oxalylcarbazole. This is probably due to the greater stability of oxalylcarbazole, on the one hand, and the comparative ease with which the derivatives containing one carbazole group in their molecule are hydrolysed, regenerating carbazole, on the other. So far as the experimental evidence goes, *N*-oxalylcarbazole cannot be regarded as an intermediate product in the formation of "carbazole-blue," prepared by the fusion of carbazole with oxalic acid (Suida, *Ber.*, 1879, **12**, 1403; Bamberger and Müller, *ibid.*, 1887, **20**, 1903).

EXPERIMENTAL.

The general method of preparation of the *N*-acyl derivatives of carbazole adopted by the author was to triturate potassium carbazole, prepared by Graebe's process (*Annalen*, 1880, **202**, 28), with a slight excess of the acid chloride; the reaction being energetic, the addition of the latter is regulated accordingly. The mixture is allowed to remain for two hours, then extracted successively with water, dilute sodium carbonate, and water again, so as to remove the potassium chloride and acidic substances, and then dried.

On triturating potassium carbazole with acetyl and benzoyl chlorides, there were obtained the *N*-acetyl and *N*-benzoyl derivatives of carbazole respectively, in the forms described by previous workers (*loc. cit.*).

The following compounds are further examples of the general reaction.

N-*Phenoxyacetylcarbazole*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>N\cdot CO\cdot CH_2\cdot OPh$.

The product of the interaction of potassium carbazole and phenoxyacetyl chloride, a pale grey powder, is soluble in all the ordinary organic solvents. It crystallises from ethyl alcohol (after decolorising the solution with animal charcoal) in white, slender needles decomposing at 121—122°, with the regeneration of carbazole.

The colourless solution of *N*-phenoxyacetylcarbazole in concentrated sulphuric acid gives with nitric acid the deep green coloration characteristic of carbazole:

0·3854 gave 15·16 c.c. N_2 at 18° and 763 mm. N=4·59.

$C_{20}H_{15}O_2N$ requires N=4·62 per cent.

N-n-*Nonoylcarbazole*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>N\cdot CO\cdot [CH_2]_7\cdot CH_3$.

The product of the reaction of potassium carbazole with *n*-nonoyl chloride is readily soluble in the usual organic solvents. It crystallised from ethyl alcohol in long, prismatic needles melting at 72—73°:

0·3266 gave 12·4 c.c. N_2 at 17° and 762 mm. N=4·42.

$C_{21}H_{25}ON$ requires N=4·56 per cent.

On heating *N*-*n*-nonoylcarbazole above its melting point, the acyl group is eliminated, decomposition also taking place on attempting to crystallise the substance from a solvent of high boiling point.

N-*Palmitylcarbazole*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>N\cdot CO\cdot[CH_2]_{14}\cdot CH_3$.

The reaction between potassium carbazole and palmityl chloride, being less energetic than those described above, is completed by keeping the mixture in an air-oven at 75° for two hours, the mixture being triturated from time to time.

The product, a grey powder, is readily soluble in all the ordinary organic solvents. The difference in solubility in hot and in cold ethyl alcohol is considerable, and the compound crystallises from this solvent in a spongy mass of small, white, matted needles melting at 90—91°. It separates from benzene in small, rhombic crystals:

0·4603 gave 12·4 c.c. N_2 at 18° and 763 mm. N=3·12.

$C_{28}H_{39}ON$ requires N=3·45 per cent.

On being heated above its melting point, the compound decomposes, carbazole being regenerated.

N-*Carbonylcarbazole*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>N\cdot CO\cdot N<\!\!\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$.

Dry carbonyl chloride was passed over finely powdered potassium carbazole, the current of gas being so regulated as to keep the temperature of the energetic reaction at 150—160°. When the reaction ceased, the product, freed from potassium chloride and acidic substances, was crystallised from ethyl alcohol, the first crop of crystals being mainly unchanged carbazole. After three crystallisations, the compound was obtained in small, white needles melting at 181—183°:

0·2805 gave 19 c.c. N_2 at 16° and 760 mm. N=7·92.

$C_{25}H_{16}ON_2$ requires N=7·78 per cent.

N-*Carbonylcarbazole* is more readily soluble than carbazole in the ordinary organic solvents.

Paschkowetzky's (*Ber.*, 1891, **24**, 2905) failure to prepare N-carbonylcarbazole by boiling potassium carbazole with carbonyl chloride in benzene solution was probably due to the low temperature. Even in boiling xylene no condensation takes place, although the reaction appears to be energetic.

N-*Oxalylcarbazole*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>N\cdot CO\cdot CO\cdot N<\!\!\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$.

The reaction between potassium carbazole and oxalyl chloride is energetic, and the operation was carried out in a manner similar

to that adopted in the case of monobasic acid derivatives of carbazole. Under these conditions, no acid of the type $>N\cdot CO\cdot CO_2H$ was formed. The crude product, freed from potassium chloride and oxalic acid, was extracted with hot alcohol to remove any unaltered carbazole. The pale grey powder is very sparingly soluble in alcohol, ether, light petroleum, chloroform, or pyridine, but somewhat more readily so in ethyl acetate, acetic acid, benzene, nitrobenzene, acetone, or carbon disulphide, and crystallises from nitrobenzene or carbon disulphide in small, white, rhombic crystals melting at 265—266°:

0·2360 gave 14·56 c.c. N_2 at 17° and 762 mm. N=7·18.
$C_{26}H_{16}O_2N_2$ requires N=7·21 per cent.

N-Oxalylcarbazole does not give with concentrated nitric acid in the presence of concentrated sulphuric acid the deep green coloration characteristic of carbazole and many of its derivatives.

It appeared to be of interest to investigate whether this substance is an intermediate product in the formation of "carbazole-blue" from carbazole and oxalic acid. To determine this, the following experiments were carried out: (1) The product of the reaction between oxalyl chloride and potassium carbazole was heated to above 200°; (2) the product of the reaction between oxalyl chloride and carbazole was heated to above 200°; and (3) oxalylcarbazole was fused with a large excess of oxalic acid and the mixture heated to above 200°.

In all these cases, no formation of "carbazole-blue" could be detected, and therefore *N*-oxalylcarbazole cannot be regarded as an intermediate product in the formation of "carbazole-blue."

The author wishes to express his indebtedness to the Department of Industrial and Scientific Research for permission to publish this work.

THE CHEMICAL DEPARTMENT,
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[*Received, September 4th,* 1918.]

LXXIV.—*The Relative Activity of certain Alkyl Iodides with Sodium α-Naphthoxide in Methyl Alcohol.*

By HENRY EDWARD COX.

THE relative activities of methyl, ethyl, and *n*-propyl iodides with sodium naphthoxides in ethyl alcohol were discussed in a previous paper (this vol., p. 666), and attention was directed to the abnormal increase in activity of methyl iodide at high dilutions. The object of the present work was to examine similarly the reaction between methyl iodide and sodium α-naphthoxide in methyl alcohol as solvent.

Menschutkin (*Zeitsch. physikal. Chem.*, 1890, **6**, 41) found that ethyl iodide and triethylamine react more rapidly in methyl alcohol than in ethyl alcohol, and ascribed this to the higher dielectric constant of the methyl alcohol. Hecht and Conrad (*ibid.*, 1889, **3**, 42) and Segaller (T., 1914, **105**, 112) have shown that sodium ethoxide and phenoxide react more rapidly in ethyl alcohol as solvent. This is surprising in view of the fact that Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474; T., 1914, **105**, 2582) have shown that in the case of the phenoxide, the activity due to ions is more than five times that due to the undissociated phenoxide. The activity would therefore be expected to be higher in the solvent of greater dissociating power, namely, methyl alcohol. Sodium α-naphthoxide, like ethoxide and phenoxide, reacts about twice as fast with the alkyl iodides in ethyl alcohol as in methyl alcohol.

EXPERIMENTAL.

The methyl alcohol was quite free from acetone, and was dehydrated over calcium oxide and calcium. The measurements were carried out at 40·0°, as described in the previous paper.

The following results were obtained with methyl iodide and sodium α-naphthoxide in equivalent concentration. The third column gives the values of k_v calculated from the equation $k_v = k_1 + a \log v$.

$a = 0·00333$.

v.	k_v (found).	k_v (calc.).
1	0·01644	0·01644
2	0·01797	0·01744
4	0·01863	0·01844
8	0·01923	0·01945
16	0·02449	0·02045
32	0·03633	0·02145
64	0·04461	0·02245

These figures show that the above equation holds as far as $v=8$, and then k_v increases abnormally rapidly, as was found to be the case in ethyl alcohol.

In order to determine whether the increase with dilution is mainly due to the change in concentration of the naphthoxide or of the methyl iodide, the following experiments were made with non-equivalent concentrations. The results are calculated from the usual formula, $k = \frac{1}{(a-b)t} \log_e \frac{b(a-x)}{a(b-x)}$, where a and b are the concentrations of iodide and naphthoxide respectively.

The results show that change in concentration of the alkyl iodide has comparatively little effect on the velocity constant, whereas the concentration of the naphthoxide has a very marked effect.

		k.
N/16-Naphthoxide;	N/4-Methyl iodide	0·02243
	N/8- ,, ,,	0·02321
	N/16- ,, ,,	0·02449
N/8-Iodide	N/8-Naphthoxide	0·01923
	N/16- ,,	0·02321
N/4-Iodide	N/4-Naphthoxide	0·01863
	N/16- ,,	0·02449

On plotting values of k against $\log v$, there is a sharp curve upwards at the point corresponding with about $v=8$. It seemed possible that at higher dilutions the reaction might not be bimolecular, but of a higher order, due to the formation of additive com-compounds, such as $C_{10}H_7 \cdot ONa, xCH_3I$, and in order to test this point, Ostwald's 'isolation' method was applied, as follows.

The reaction velocity may be represented by the equation $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 are concentrations of naphthoxide and iodide respectively. In the following experiments, c_2 is large compared with c_1, and is taken as constant during that part of the reaction measured; the equation then takes the form $-dc_1/dt = k_1 c_1^m$, where $k_1 = kc_2^n$. The order of reaction is then equal to m.

Experiment I. N/16-Naphthoxide. N/1-Iodide.

t.	c.	$1/t \log c_0/c$.
0	6·45	—
30	3·70	0·00804
55	2·35	0·00797
65	2·00	0·00786
75	1·62	0·00800

Mean $k_1' = 0·00797$

Experiment II. N/16-Naphthoxide. N/4-Iodide.

t.	c.	$1/t \log c_0/c$.
0	7·30	—
66	5·10	0·00236
83	4·75	0·00225
106	4·20	0·00226
148	3·50	0·00217

Mean $k_1'' = 0·00224$

Experiment III. N/16-Naphthoxide. N/8-Iodide.

t.	c.	$1/t \log c_0/c$.
0	7·60	—
77	6·10	0·00124
96	5·80	0·00122
130	5·35	0·00117
160	4·95	0·00116

Mean $k_1''' = 0·00120$

The values of k_1 are sufficiently constant to show that the reaction is unimolecular with regard to the naphthoxide.

If k_1' and k_1'' are values of k_1 from two experiments in which the concentration of naphthoxide is initially the same, whilst that of the methyl iodide is varied and equal to c_2' and c_2'', then $k_1' = kc'^n_2$ and $k_1'' = kc''^n_2$, hence $n = \log\frac{k_1'}{k_1''}\Big/\log\frac{c_2'}{c_2''}$. Substituting the values obtained in experiments I, II, and III, $n = 0·92$, $0·91$, $0·90$, which indicates that n approaches the value unity. The reaction is therefore unimolecular with respect to methyl iodide, and the whole reaction is bimolecular at all dilutions from $N/1$ to $N/64$.

Effect of the Products of Reaction on the Velocity Coefficient.

Arrhenius, and more recently Senter, have pointed out that velocity coefficients often exhibit a tendency to fall off as the experiment proceeds, owing to the action of the salts formed during the reaction. As the constants in the reactions here considered show this tendency to diminish, the following experiments were made with an addition of anhydrous sodium iodide and α-naphthyl methyl ether respectively.

$N/8$-Sodium α-naphthoxide and $N/8$-methyl iodide.	k.
No sodium iodide	0·01923
$N/4$,, ,,	0·01929
$N/8$,, ,,	0·01907
$N/8$ α-Naphthyl methyl ether	0·01690
$N/4$-Naphthoxide and $N/4$-methyl iodide.	
No α-Naphthyl methyl ether	0·01863
$N/4$- ,, ,, ,,	0·01535

These results show that whilst sodium iodide has no appreciable influence on the velocity coefficient, the formation of the ether greatly retards the velocity, and this probably accounts for the observed falling off of the velocity constant.

It is still unexplained why the velocity is practically constant throughout any one experiment, although the concentration falls to less than one-half of its initial value, whereas if an experiment is commenced at a lower concentration, the velocity coefficient is considerably increased in accordance with the equation $k_v = k_1 + a \log v$.

Ethyl and n-*Propyl Iodides.*

These iodides react more slowly than methyl iodide, and the equation $k_v = k_1 + a \log v$ is found to hold to as high a dilution as it was practicable to measure.

The results of three experiments are as follows:

	Ethyl iodide.		n-Propyl iodide.	
v.	k_v (found).	k_v (calc.).	k_v (found).	k_v (calc.).
1	0·005350	0·005350	0·002355	0·002355
8	0·006026	0·005982	0·003071	0·003077
32	0·006280	0·006403	0·003601	0·003559
	$a=0·00070$		$a=0·00080$	

The relative activities of the three iodides at concentration $N/1$ are:

Solvent :—	Methyl alcohol.	Ethyl alcohol.
Methyl iodide	6·98	9·55
Ethyl iodide	2·27	2·14
n-Propyl iodide	1·00	1·00

and the ratio of the velocity coefficients in these two solvents is:

	Methyl iodide.	Ethyl iodide.	*n*-Propyl iodide.
Methyl alcohol ...	1·00	1·00	1·00
Ethyl alcohol......	2·50	1·71	1·83

These figures agree very closely with the results of Hecht and Conrad and of Segaller for sodium ethoxide and phenoxide.

Summary and Conclusions.

(1) The reaction between methyl iodide and sodium α-naphthoxide is bimolecular at all dilutions from $N/1$ to $N/64$. The velocity coefficient increases with dilution in accordance with the equation $k_v=k_1+a\log v$ as far as $v=8$, and thereafter it increases more rapidly.

(2) The effect of varying the concentration of the alkyl iodide is comparatively small, but the initial concentration of the naphthoxide has a very marked effect on the velocity coefficient.

(3) Sodium iodide has no effect on the velocity coefficient.

(4) α-Naphthyl methyl ether greatly retards the reaction.

(5) The velocity of reaction of the alkyl iodides is approximately twice as great in ethyl alcohol as in methyl alcohol.

(6) The relative activity of the first three members of the series is in the order methyl, ethyl, *n*-propyl iodide, and methyl iodide is much more active than the others.

I wish to express my thanks to Mr. G. R. Thompson for providing every facility for this work, and to Dr. J. C. Crocker for his interest and advice.

DOCK STREET,
NEWPORT, MON.

[*Received, August 29th*, 1918.]

LXXV.—*The Hydrolysis of Soap Solutions, Measured by the Rate of Catalysis of Nitrosotriacetonamine.*

By JAMES WILLIAM MCBAIN and THOMAS ROBERT BOLAM.

THE concentration of hydroxyl ion in soap solutions was measured by McBain and Martin (T., 1914, **105**, 957) by the electromotive force method, and the measurements recorded in the present paper agree with those results in showing that the concentration of hydroxyl ion is only of the order of magnitude of $N/1000$. It is therefore impossible to attribute the conductivity of soap solutions to free hydroxyl ions. For the evidence with regard to the existence and nature of the ionic micelle and their bearing on the conductivity, reference should be made to other communications from this laboratory.*

Method of Measurement.

The method employed was the rate of catalysis of the reaction

$$CO<\begin{matrix}CH_2\cdot CMe_2\\ CH_2\cdot CMe_2\end{matrix}>N\cdot NO \longrightarrow H_2O + N_2 + CO<\begin{matrix}CH:CMe_2\\ CH:CMe_2\end{matrix},$$

as shown by Francis and his collaborators (T., 1912, **101**, 2358; 1913, **103**, 1722; 1915, **107**, 1651). The reaction is unimolecular and the velocity is proportional to the concentration of hydroxyl ion. The volume method had been found to be accurate to within about 2 or 3 per cent. at the ordinary temperature.

The results are calculated according to the system proposed by McBain (*Trans. Faraday Soc.*, 1917, **13**, 1), which consists in always setting the rate constant equal to unity and in choosing the unit of time accordingly.

The formula used here is consequently

$$T = 2{\cdot}303 \log \frac{A}{A-x},$$

instead of the hitherto customary

$$k = \frac{2{\cdot}303}{t} \log \frac{A}{A-x}$$

where k is the rate constant. The disadvantages of the system hitherto employed, as compared with that proposed, are illustrated

* McBain and Taylor, *Ber.*, 1910, **43**, 321; *Zeitsch. physikal. Chem.* 1911, **76**, 179; Bowden, T., 1911, **99**, 191; McBain, Cornish, and Bowden, T., 1912, **101**, 2042; Bunbury and Martin, T., 1914, **105**, 417; McBain and Martin, T., 1914, **105**, 957; Laing, T., 1918, **113**, 435; McBain and Salmon, *J. Amer. Chem. Soc.*, 1918; McBain, *J. Soc. Chem. Ind.*, 1918, **37**, 249 (a brief summary).

by the rate of reaction in the presence of 0·0138N-OH′ at 40·0°. The rate constant is 0·0708. This statement is meaningless until the further information is given that "time has been measured in minutes." Under the new system, this becomes—"the time unit is 14·1 minutes"—a statement which is much more readily visualised, is self-contained, and does away with small decimals. It further means, in the case of unimolecular reactions such as the present, that the reaction requires 14·1 minutes to proceed to the extent of 63·2 per cent.

Determinations were made at 30°, 40°, 70°, and 90°. The values of the time units for definite concentrations of hydroxyl ion at each temperature were measured by observing the rate in solutions of sodium hydroxide. These solutions were made up from sodium and boiled-out conductivity water, and all vessels were carefully flushed out with air freed from carbon dioxide. Soap solutions were made up in silver vessels as described in previous communications. The reaction was carried out in a Jena-glass flask containing a small glass tube, which could be dropped into the solution in the flask when it was desired that the reaction should commence. In some cases this tube contained the soap solution, in others the solution of nitrosotriacetonamine. 0·1300 Gram of that substance was employed in each case. The amount of gas which should have been evolved, saturated with water vapour at about 18°, is 17·18 c.c.; as a matter of fact, on the average about 8 per cent. more than this was evolved. Francis and Clibbens state that they obtained values within 2·5 per cent. of the theoretical volume. Hence the "infinity reading" was taken after a period five times as long as that required for the production of 9·3 c.c. of nitrogen.

The results for sodium hydroxide are given in table I, in the final column of which the product of "time unit" and concentration is recorded. This should be a constant for each temperature, and is also equal to the reciprocal of the older expression k/OH'. The final products for 40°, 70°, and 90° are 0·196, 0·0236, and 0·00545, respectively. The degree of accuracy is much less at the higher temperatures, owing to the great speed of the reaction and the very low concentrations of hydroxyl ion, which alone are measurable. Further, the solubility of the glass and difficulties due to vaporisation and fluctuations of temperature play an increasing rôle. However, none of these influences vitally affects the value of the results, on account of the fact that the hydrolysis of the soaps is itself so small.

TABLE I.

Rate of Catalysis in Solution of Sodium Hydroxide.

Temperature.	Concentrations.		Number of experiments.	Time units T minutes.			
	$NaOH_{18°}$	$OH'=C$.		Max.	Min.	Mean.	C.T.
40°	0·0146	0·0139	4	14·4	13·5	14·1	0·196
70	0·00314	0·00302	4	8·32	6·80	7·67	0·0232
,,	0·00392	0·00396	2	6·52	6·45	6·49	0·0244
90	0·000654	0·000626	2	9·43	9·01	9·22	0·00579
,,	0·000785	0·000757	2	7·69	7·46	7·57	0·00569
,,	0·000796	0·000766	2	6·41	6·33	6·37	0·00488

The temperature coefficient of the reaction above 40° is 2·02 and 2·04, depending on whether the time unit at 70° or 90° is taken for the calculation. This is in general agreement with the results previously and subsequently obtained (T., 1915, **107**, 1657), showing that the temperature coefficient diminishes with rise of temperature.

Applicability of the Method.

In view of the low values of hydroxyl ion obtained for soap solutions, it was considered advisable to carry out a few experiments in order to determine the neutral salt action, if any, of the sodium salt by the lowest fatty acid of this series, namely, sodium acetate.

The results of two series of experiments are given in table II, where concentrations are expressed in volume normality at 90°. The first column gives the preparation used (A being sodium acetate made anhydrous by heating in an air-bath at 125°, C and D being ordinary crystals weighed either dry or moist after recrystallisation and subsequently analysed, thus avoiding any slight loss of acetic acid through heating), the last column being the apparent hydroxyl-ion concentrations as deduced from the factors obtained from table I.

TABLE II.

Sodium Acetate at 90° with and without Sodium Hydroxide.

NaAc.	Concentrations.		Number of experiments.	Time units minutes.			
	NaAc.	NaOH.		Max.	Min.	Mean.	$(OH')_v$.
D, C	0·923	—	2	28·1	25·5	26·8	0·000203
A	0·967	—	2	25·0	24·4	24·7	0·000221
C, D	0·923	0·000759	3	10·4	9·0	9·81	0·000556
A	0·967	0·000759	2	9·7	8·9	9·32	0·000585

These results require elucidation, for there are two factors involved, namely, neutral salt action and hydrolytic equilibrium. Taking first hydrolysis, calculation shows that the observed rate of catalysis would indicate a rather high value, $60—70 \times 10^{-14}$, for K_w, the dissociation constant of water at 90°. The latter is still uncertain as between the limits $33—70 \times 10^{-14}$. With the present method, dilute solutions would have to be employed to minimise neutral salt action.

The nature of the neutral salt action follows from the experiments in table II, employing added sodium hydroxide. The sodium hydroxide added will, of course, be only moderately dissociated in accordance with the principle of isohydrism. The total rate predicted will consequently be less than that of the hydroxide when taken alone, in spite of the influence of hydrolysis. Taking one set of assumptions in the preceding paragraph, the hydroxyl ion predicted is about 0·000614 for both the 0·923 and 0·967*N*-solutions containing sodium hydroxide. Taking another set, using osmotic data, this number becomes about 0·000571, which is identical with the mean of the observed value in table II.

This suffices to show that sodium acetate in normal solution does not exhibit any accelerating neutral salt effect. If it has any effect, it retards the reaction by anything up to 6 per cent., which is within the experimental error for the calculation above.

A much more vital effect would be if the soap in concentrated solutions sorbs nitrosotriacetonamine, thus cutting down the effective concentration at any time, and therefore the rate. The reaction would proceed to completion, for the whole of the amine would be liberated progressively, but the apparent rate would be proportionately less than that corresponding with the real concentration of hydroxyl ion. The whole of the nitrogen is actually evolved.

If this phenomenon occurs, it would be of importance only in concentrated solutions, where the soaps exist as colloidal electrolytes. There the apparent concentration of hydroxyl ion would be too small, whereas in dilute solutions, in which the soaps exist essentially as simple electrolytes, normal values would be observed. This is just what is found when the results from the present method are compared with those from the determination of electromotive force (*loc. cit.*). The values are nearly identical up to *N*/20-solution, but at N/10-solution they begin gradually to diverge until at 0·8*N*-solution the alkalinity measured by catalysis is only a fraction of that found by the method of electromotive force.

The only uncertainty in the measurements from electromotive

force is in calculating the diffusion potential. If the difference between the methods is to be ascribed to this source, it would make the hydrolysis much smaller even than that deduced, which was one or two tenths of a per cent. This establishes even more conclusively the main result of the previous paper. This assumption, however, predicates that the palmitate micelle possesses only low equivalent mobility, whereas the high observed conductivity necessitates the opposition conclusion. If sorption is taken into account, the results obtained by the catalytic method confirm those derived from electromotive force.

Direct proof of the occurrence of sorption in concentrated solution is obtained by adding a known amount of sodium hydroxide to the soap and observing that the effect on the rate is abnormally low. This is not due to sorption of the hydroxyl ion by the soap, as both electromotive force data (*loc. cit.*) and other evidence show that basic soaps are not formed. Experiments of this kind are set forth in table III. The concentrations of sodium palmitate are given in weight normality, the sodium hydroxide in volume normality at 90°. Two experiments from table I are added for comparison. The results show strikingly that the apparent rate is much lower than that corresponding with the alkali present and added, which points to sorption of amine by soap in concentrated solution as the explanation of the low rate. It should be remembered, of course, that in these soap solutions the concentration of sodium ions is about 0·30 weight normal, or about 0·25 volume normal at 90°, so that the sodium hydroxide is not fully dissociated and the hydrolysis of the soap has been partly repressed. Even so, the observed rate is but a fraction of that expected.

The last three lines of table III present experiments carried out by J. C. Pope in June, 1918, using a special preparation of sodium palmitate, which, although discoloured, was found to be very slightly alkaline in 90 per cent. alcoholic solution. The rate in mixtures containing considerable excess of alkali is about six times less than if the soap had been absent. This confirms the conclusions already drawn and reconciles the results of the catalytic and electromotive force methods set forth in table IV.

TABLE III.

0·8 Sodium Palmitate at 90° with and without Sodium Hydroxide.

Concentration.		Number of experiments.	Time units minutes.			(OH′).
NaP.	NaOH.		Max.	Min.	Mean.	Deduced.
0·8	—	3	25·0	19·9	21·6	0·000252
,,	0·000774	3	20·7	18·9	19·8	0·000275
—	0·000785	2	7·69	7·46	7·57	0·000784
1·0	—	2	15·0	14·8	14·9	0·000266
,,	0·00374	1	—	—	8·09	0·000614
,,	0·0187	1	—	—	1·75	0·00312

Results with Soap Solutions.

Measurements on solutions of pure palmitate have been carried out at 30°, 40°, 70°, and 90°. The results for sodium palmitate are given in table IV, and those for potassium palmitate in table V.

TABLE IV.

Alkalinity of Solutions of Sodium Palmitate.

Temperature.	Concentration: weight normality.	Number of experiments.	Time units minutes. Max.	Min.	Mean.	$(OH')_v$.	Hydrolysis, per cent.	By E.M.F., per cent.
70°	0·046	4	43·7	42·0	42·8	0·000438	0·99	—
,,	0·101	2	43·5	42·6	42·0	0·000561	0·59	—
90	0·042	2	6·02	5·98	6·0	0·000908	2·24	2·3
,,	0·50	2	27·0	27·0	27·0	0·000202	0·05	0·37
,,	0·8	3	25·0	19·9	21·6	0·000252	0·04	0·28

TABLE V.

Alkalinity of Solutions of Potassium Palmitate.

Temperature.	Concentration: weight normality.	Number of experiments.	Time units minutes. Max.	Min.	Mean.	$(OH')_v$.	Hydrolysis, per cent.	by E.M.F., per cent.
30°	0·050	2	561·6	520·6	541·1	0·00097*	2·04	—
40	0·051	2	598·8	431·0	514·9	0·000391	0·82	—
70	0·050	3	43·7	42·6	43·1	0·000545	1·14	—
,,	0·100	2	38·8	38·3	38·5	0·000612	0·65	—
,,	0·85	4	409·9	380·2	395·1	0·0000594	0·009	—
90	0·019	3	7·4	7·0	7·2	0·000757	4·1	5·7
,,	0·042	2	6·06	5·7	5·9	0·000928	2·3	2·2
,,	0·1	4	6·1	5·7	5·9	0·000927	0·99	1·25
,,	0·302	5	12·7	6·1	9·4	0·000580	0·22	0·64
,,	0·85	1	—	—	49·5	0·000110	0·017	0·27

* These experiments were carried out by F. H. Geake by the pressure method. As the solutions have begun to be heterogeneous the alkalinity is, as expected, greater than at the higher temperatures where it is liquid. Compare McBain and Martin, *loc. cit.*, p. 975.

The seventh column gives the concentration of hydroxyl ion deduced, neglecting the effect of sorption of amine, and in the eighth the percentage hydrolysis found by electromotive force measurements (*loc. cit.*) is added for comparison.

Comparison of the last two columns in tables IV and V brings out the agreement of the two methods for dilute solutions, whilst the divergence in the concentrated solution is due to sorption of amine by the colloidal soap, as already explained.

The tables show at once that the alkalinity of all soap solutions is low and cannot account for more than a few per cent. of the conductivity of soaps except in very dilute solutions. However, it is quite sufficient to exclude the existence of free palmitic acid in soap solutions except in very minute amount (see McBain and Martin, *loc. cit.*, p. 973). Since the concentration of the hydroxyl ion exceeds $0{\cdot}00002N$ in the case of every soap solution, even when containing excess of fatty acid, all higher fatty acids which are formed or added must exist in the form of acid soap, that is, in solid solution, adsorbed or chemically combined, but not in the free condition, except to an immeasurably small extent. This combats a very prevalent error (see, for instance, Washburn, "Principles of Physical Chemistry," 1915, p. 379).

Potassium palmitate when studied by the method of electromotive force exhibits a maximum alkalinity equal to $0{\cdot}000316N$ in $0{\cdot}5N$-solution, diminishing to a quarter of this value in $1{\cdot}00N$-solution, which corresponds with only $0{\cdot}08$ per cent. hydrolysis. The data for sodium palmitate were less definite, but it was shown (*loc. cit.*, p. 973) that the values in concentrated solution tend to be too high. This effect also helps to explain the divergence between the two methods in concentrated solutions. The falling off in absolute alkalinity is quite simply explained on the basis of McBain and Salmon's theory of colloidal electrolytes (*J. Amer. Chem. Soc.*, 1918), for in concentrated solutions the palmitate ions largely disappear, being displaced by the ionic micelle.

A word is necessary with regard to what we have called "hydrolysis, per cent.," in the last two columns of tables IV and V, for which we have been criticised by Bancroft (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 184). Bancroft's criticism arises from our having regarded alkalinity (concentration of hydroxyl ion) as hydrolysis. The difference is largely a matter of words and of point of view. His contention is that the hydrolysis may have been anything up to 100 per cent., but that the hydroxyl ion has been immediately and almost quantitatively sorbed by the resulting acid palmitate (it cannot be palmitic acid, and the colloidal sodium palmitate must contain all the excess of palmitic acid liberated).

McBain and Martin's paper contains direct measurements of the alkalinity of sodium hydroxide in the presence of soap; the hydroxide shows no appreciable sorption by soap; this is direct experimental evidence which has apparently not been considered by Bancroft, and would appear to be conclusive.

Summary.

Rate of catalysis, like electromotive force, shows that soap solutions are definitely, although very slightly, alkaline.

This alkalinity decreases with falling temperature, but is increased again when the solution solidifies or becomes heterogeneous.

The concentration of hydroxyl ion observed in all cases is sufficient to exclude the widely held view of the possibility of the existence of appreciable amounts of free fatty acid in any soap solution. Instead, acid soap must be formed in which practically all the excess of fatty acid is sorbed or combined.

The experiments here communicated are taken from a series that had to be discontinued in July, 1914. Our thanks are due to the Colston Society of the University of Bristol for a grant which has defrayed the expenses of this investigation.

CHEMICAL DEPARTMENT,
BRISTOL UNIVERSITY. [*Received, September 4th*, 1918.]

LXXVI.—*Studies in the Phenylsuccinic Acid Series. Part VII. The Action of Alcohols and Amines on* r-*Diphenylsuccinic Anhydride.*

By HENRY WREN and HOWELL WILLIAMS.

THE present investigation was undertaken with the primary object of ascertaining whether derivatives of *meso*diphenylsuccinic acid are produced during the reaction of alcohols and amines with *r*-diphenylsuccinic anhydride. It has been pointed out previously by Anschütz and Bendix (*Annalen*, 1890, **259**, 73) that the *r*-anhydride is converted by hot water into a mixture of the *r*-acid (about 96 per cent.) and *meso*-acid (about 4 per cent.), and this result is corroborated by the observation of Wren and Still (T., 1915, **107**, 1451) that the optically active anhydrides, when treated

with hot water, pass into diphenylsuccinic acids of the same sign containing about 8 per cent. of optically inactive material, from which *meso*diphenylsuccinic acid can be isolated in very small quantity. The action of cold ethyl alcohol on the *l*-anhydride gave a rather more complex result. About 20 per cent. of inactive material appeared to be present in the crude product, from which however, a homogeneous substance could not be isolated; after crystallisation from light petroleum, a small quantity of substance was obtained which was not completely molten below 146°. Since ethyl hydrogen *l*-diphenylsuccinate melts at 113·5—114·5°, whilst Franchimont (*Ber.*, 1872, **5**, 1050) gave 140° as the melting point of the corresponding *r*-ester, it seemed valid to conclude that ethyl hydrogen *meso*diphenylsuccinate was also present. A not dissimilar result is recorded by Anschütz and Bendix (*loc. cit.*), who, by shaking *r*-diphenylsuccinic anhydride with chloroform containing ethyl alcohol, obtained a product analyses of which gave results in agreement with those required for the ethyl hydrogen ester, but the physical constants (melting point of crop, 164—168°; melting point of substance from mother liquor, 156—174°) appeared to show that the material was not uniform.

The experiments just quoted pointed thus to a very profound influence of the reagent on the mode of opening of the anhydride ring, but their significance was greatly discounted by the incidental observation that ethyl hydrogen *r*-diphenylsuccinate melts at 170—171° instead of at 140°, as recorded by Franchimont. The action of *r*-diphenylsuccinic anhydride on methyl and ethyl alcohols, on aniline, and on *p*-toluidine has therefore been studied, with the result that in the case of ethyl alcohol only has any definite evidence of the formation of *meso*-derivatives been obtained, and even in this instance the amount is very small.

The interaction of *r*-diphenylsuccinic anhydride and aniline has been studied by Anschütz and Bendix (*Annalen*, 1890, **259**, 92), who prepared diphenylsuccinanil by heating the anhydride with half its weight of aniline at 170—175°; on treatment with a boiling aqueous solution of barium hydroxide, the anil was converted into a diphenylsuccinanilic acid which melted at 220°. By the action of the anhydride on aniline dissolved in benzene, they isolated a substance which melted at 65—68°, resolidified at 105—108°, and again melted at 220°. A repetition of the latter experiment has led to a somewhat different result, since we find the crude product to melt at 173—176°, to resolidify at about 187°, and to melt again at 226°, the initial melting point, however, being somewhat dependent on the conditions of the determination; after purification, it yields a diphenylsuccinanilic acid

which melts at 173—175° with the evolution of gas, then re-solidifies, and again melts at 227°. This appears to be practically the sole product of the change. It is readily transformed into diphenylsuccinanil either by the action of heat or by ethyl-alcoholic hydrogen chloride. Considering the conditions of their formation, it appears not unreasonable to regard the product melting at 173—175° as derived from the *r*-acid and that melting at 220° as belonging to the *meso*-series.

r-Diphenylsuccinic anhydride reacts very readily with a solution of *p*-toluidine in benzene, giving an almost quantitative precipitate of an acid melting at 195—196°, which appears to be the sole product of the action. This acid yields a barium salt which is sparingly soluble in water; it is readily transformed by the action of heat or of alcoholic hydrogen chloride into diphenylsuccino-*p*-tolil. The latter substance is converted by alkali into a mixture of acids which can be separated by taking advantage of the widely differing solubilities of their barium salts in water; from the less readily soluble portion, the acid melting at 195—196° can easily be isolated, whilst the more readily soluble portion yields an isomeric acid melting and decomposing at 206°, which is easily converted into diphenylsuccino-*p*-tolil. From the mode of formation, the relatively lower melting point and sparing solubility of the barium salt, it appears reasonable to conclude that the former acid belongs to the racemic series, the latter being therefore a derivative of the *meso*-type.

EXPERIMENTAL.

Partial Esterification of r- *and* meso-*Diphenylsuccinic Acids.*

Ethyl hydrogen *meso*diphenylsuccinate was obtained from the products of the incomplete esterification of the *meso*-acid by ethyl alcohol and sulphuric acid according to the Fischer-Speier method. Isolation was readily effected by shaking the crude product, obtained after removal of excess of alcohol, with water and chloroform, whereby unchanged *meso*-acid remained undissolved. The chloroform solution was agitated with concentrated sodium carbonate solution; the latter, when acidified, yielded an immediate precipitate of ethyl hydrogen *meso*diphenylsuccinate, which was purified by crystallisation from slightly aqueous alcohol and subsequently from benzene.

Ethyl hydrogen meso*diphenylsuccinate* separates from benzene in minute, colourless needles. It is readily soluble in cold chloroform or ether or in hot ethyl alcohol, and moderately so in cold ethyl alcohol. When heated, it shrinks to a thin core and melts

sharply at 174·5—175°. After being dried in a vacuum over calcium chloride, the ester retains half a molecule of water:

0·1461 gave 0·3765 CO_2 and 0·0816 H_2O. C=70·3; H=6·3.

0·5431 lost 0·0149 at 100—105°. H_2O=2·74.

0·1393 * gave 0·3700 CO_2 and 0·0756 H_2O. C=72·4; H=6·1.

0·3885 neutralised 12·9 c.c. of 0·1033 *N*-sodium hydroxide. Calc.: 12·64 c.c.

$C_{18}H_{18}O_4,\frac{1}{2}H_2O$ requires C=70·3; H=6·3; H_2O=2·93 per cent.

$C_{18}H_{18}O_4$ requires C=72·5; H=6·1 per cent.

Ethyl hydrogen *r*-diphenylsuccinate was similarly obtained by the incomplete esterification of *r*-diphenylsuccinic acid, and was purified through the sparingly soluble sodium salt, and finally by cautious crystallisation of the acid ester from a small quantity of ethyl alcohol. It may be more readily crystallised from aqueous alcohol or from a mixture of benzene and light petroleum (b. p. 80—100°), but the removal of small quantities of admixed *r*-acid is not easily accomplished in this manner.

Ethyl hydrogen r-*diphenylsuccinate* separates from alcohol in aggregates of ill-defined needles; it is readily soluble in the boiling, fairly readily so in the cold solvent. It dissolves readily in cold ether, fairly readily in cold benzene, sparingly in light petroleum. It melts at 170—171°:

0·4137 neutralised 13·9 c.c. of *N*/10-potassium hydroxide. Calc.: 13·88 c.c.

0·1725 gave 0·4575 CO_2 and 0·0944 H_2O. C=72·3; H=6·1.

$C_{18}H_{18}O_4$ requires C=72·5; H=6·1 per cent.

On complete esterification with ethyl alcohol and sulphuric acid, the acid ester was converted into ethyl *r*-diphenylsuccinate melting at 84·5—85·5°, thus confirming the position of the ester in the racemic series.

Sodium ethyl r-*diphenylsuccinate* separates from water, in which it is sparingly soluble at the ordinary temperature, in aggregates of fine needles:

0·2188 † lost 0·0395 at 100—110°. H_2O=18·05.

$C_{18}H_{17}O_4Na,4H_2O$ requires H_2O=18·37 per cent.

0·1788 ‡ gave 0·0386 Na_2SO_4. Na=6·89.

$C_{18}H_{17}O_4Na$ requires Na=7·20 per cent.

The salt evolved acrid fumes and became discoloured at 180°.

Barium ethyl r-*diphenylsuccinate* was prepared by neutralising a suspension of the ethyl hydrogen ester in water with barium hydroxide solution; it is moderately soluble in cold water:

* Dried at 100–105° until constant in weight.

† Air-dried. ‡ Dried at 100–110°.

0·3754 * lost 0·0177 at 100—110°. $H_2O = 4·72$.

$C_{36}H_{34}O_8Ba,2H_2O$ requires $H_2O = 4·70$ per cent.

0·2034 † gave 0·0662 $BaSO_4$. Ba = 19·12.

$C_{36}H_{34}O_8Ba$ requires Ba = 18·78 per cent.

Action of Ethyl Alcohol on r-*Diphenylsuccinic Anhydride.*

r-Diphenylsuccinic anhydride (8·1 grams) was allowed to remain in a stoppered flask, with occasional shaking, with ethyl alcohol (100 c.c.) until solution was complete, for which about three days were required. (A small portion of the solution was evaporated to dryness, and the residue was titrated with standard sodium hydroxide solution; the results indicated that the ethyl hydrogen ester contained a very small proportion of the free acid. This experience was confirmed in a number of other instances, and it therefore appears to be a matter of very considerable difficulty to prepare the alcohol absolutely free from moisture and to maintain it in this condition during the experiment.) The alcoholic solution was concentrated and exactly neutralised with aqueous-alcoholic sodium hydroxide solution. After complete removal of the alcohol, the aqueous solution was cooled, when sodium ethyl *r*-diphenylsuccinate was readily deposited (crop *A*). The precipitate was removed, and a second small crop of crystals was obtained by concentrating the filtrate. The mother liquor from the latter crop was acidified with hydrochloric acid and extracted with ether. The ethereal extract, after evaporation, left a small residue which melted indefinitely at 148—200°. It was completely esterified with ethyl alcohol and sulphuric acid; the mixture of normal esters was crystallised from ethyl alcohol, when ethyl *meso*diphenylsuccinate (about 0·4 gram) was obtained in well-defined needles which melted at 140—141°.

The crop *A* (see above) was decomposed with dilute hydrochloric acid; the precipitated acid ester (6·8 grams) melted sharply at 170—171°, and was in all respects identical with ethyl hydrogen *r*-diphenylsuccinate obtained by partial esterification of the *r*-acid.

Action of Methyl Alcohol on r-*Diphenylsuccinic Anhydride.*

r-Diphenylsuccinic anhydride (5 grams) was warmed with absolute methyl alcohol (40 c.c.) at 40° during six hours. The mixture was cooled and the precipitated acid ester removed; it melted at 196—198°, and proved to be pure methyl hydrogen *r*-diphenylsuccinate. The material obtained by evaporation of the filtrate melted at 194—198°; the esterification of the latter was completed

* Air-dried. † Dried at 100–110°.

as usual, but the only substance which could thus be isolated was methyl *r*-diphenylsuccinate.

Methyl hydrogen r-*diphenylsuccinate* separates from hot methyl alcohol, in which it is sparingly soluble, in small pyramids. It dissolves sparingly in boiling benzene, moderately readily in cold ether. It melts at 196—198° after slight previous sintering:

0·3303 neutralised 17·45 c.c. of 0·0666 *N*-alkali. Calc.: 17.47 c.c.

0·1847 gave 0·4878 CO_2 and 0·0948 H_2O. C=72·0; H=5·7.

$C_{17}H_{16}O_4$ requires C=71·8; H=5·7 per cent.

The *sodium* salt separates from its aqueous solution in small prisms:

0·4456 * lost 0·0962 at 100—110°. H_2O=21·6.

$C_{17}H_{15}O_4Na,4H_2O$ requires H_2O=19·05 per cent.

0·1690 † gave 0·0385 Na_2SO_4. Na=7·37.

$C_{17}H_{15}O_4Na$ requires Na=7·50 per cent.

Action of Aniline on r-*Diphenylsuccinic Anhydride.*

A solution of the *r*-anhydride (5 grams) in benzene (10 c.c.) was added to aniline (1·85 grams) dissolved in the same solvent (15 c.c.); in the course of a few seconds, a copious, white precipitate commenced to separate, and the solution speedily became semi-solid. The *r*-diphenylsuccinanilic acid, which was almost quantitatively precipitated, melted at 168—169°, resolidified, and again melted at 226·5—229°. It was crystallised from a small quantity of warm alcohol.

r-*Diphenylsuccinanilic acid* separates from alcohol in short prisms. It is readily soluble in warm alcohol or benzene, in cold ether or acetone, less readily so in carbon tetrachloride or light petroleum. It dissolves sparingly in cold alcohol or benzene. It melts and evolves gas at 173—175°, resolidifies at a slightly higher temperature, and again melts at 227°; the observed values depend somewhat on the rate of heating and the diameter of the tubes used:

0·1853 gave 0·5163 CO_2 and 0·0939 H_2O. C=76·0; H=5·7.

0·3721 „ 13·6 c.c. N_2 at 16° and 765 mm. N=4·3.

$C_{22}H_{19}O_3N$ requires C=76·5; H=5·5; N=4·1 per cent.

Conversion of r-*Diphenylsuccinanilic Acid into Diphenylsuccinanil.*

A. *By the Action of Heat.*—*r*-Diphenylsuccinanilic acid was gradually heated to 230°, when complete fusion was obtained. The substance solidified, when cooled, to a pale yellow mass which,

* Air-dried. † Dried at 100–110°.

after being crystallised from benzene, yielded fine, colourless needles; these were identified as diphenylsuccinanil from the melting point (229—230° after slight shrinkage at 227°) and analysis (Found: C=80·9; H=5·2. Calc.: C=80·7; H=5·2 per cent.). Anschütz and Bendix (*loc. cit.*) describe the substance as separating from benzene in fine, colourless needles which melt at 226—227°, from acetic acid in larger, shining needles melting at 230—231°.

B. *By the Action of Ethyl-alcoholic Hydrogen Chloride.*—The acid (1·1 grams) was gently warmed with a 3 per cent. solution of hydrogen chloride in ethyl alcohol; it did not immediately dissolve, but, on reaching the boiling point, a copious, crystalline precipitate speedily separated. Boiling was continued during four hours, during which no change in the appearance of the product was observed. The alcohol was removed, and the residue crystallised from benzene, when diphenylsuccinanil (0·7 gram) melting at 229—230° was readily obtained.

The behaviour of *r*-diphenylsuccinanilic acid under these conditions is thus similar to that of the anilic acid, melting at 220°, described by Anschütz and Bendix.

Action of p-*Toluidine on* r-*Diphenylsuccinic Anhydride.*

Molecular quantities of *r*-diphenylsuccinic anhydride and of *p*-toluidine were dissolved in benzene and mixed; after a few seconds, the solution became cloudy, and in the course of a few minutes, *r*-diphenylsuccino-*p*-toluidic acid was almost quantitatively precipitated. The crude substance melted and evolved gas at 194—196°. It was crystallised from slightly aqueous alcohol.

r-*Diphenylsuccino*-p-*toluidic acid* separates from aqueous alcohol in small needles. It is readily soluble in hot alcohol, sparingly so in hot benzene, and very sparingly so in hot water; it dissolves readily in cold acetone or ether, less readily in cold chloroform. It melts at 195—196° and does not appear to suffer decomposition below 270°:

0·1613 neutralised 6·8 c.c. of 0·0666 *N*-alkali. Calc.: 6·75 c.c.
0·1850 gave 0·5229 CO_2 and 0·0960 H_2O. C=77·1; H=5·8.
0·3842 ,, 12·8 c.c. N_2 at 18° and 762 mm. N=3·95.

$C_{23}H_{21}O_3N$ requires C=76·9; H=5·9; N=3·90 per cent.

At its melting point, *r*-diphenylsuccino-*p*-toluidic acid loses water and passes into the tolil (see later). With slightly impure specimens of the acid, this decomposition is very evident, and water vapour is freely evolved. With the pure acid, however, some external impulse appears requisite to render this effect manifest.

Silver r-*diphenylsuccino*-p-*toluidate* forms a voluminous, white powder:

0·3275 gave 0·0744 Ag. Ag = 22·72.
$C_{23}H_{20}O_3NAg$ requires Ag = 23·16 per cent.

Methyl r-*diphenylsuccino*-p-*toluidate* was prepared by the action of an excess of methyl iodide on dry silver diphenylsuccino-*p*-toluidate, and was purified by crystallisation from a small quantity of ethyl alcohol, from which it separates in well-defined, microscopic needles melting at 173—174·5°:

0·1395 gave 0·3923 CO_2 and 0·0807 H_2O. C = 76·7; H = 6·5.
$C_{24}H_{23}O_3N$ requires C = 77·2; H = 6·2 per cent.

Conversion of r-*Diphenylsuccino*-p-*toluidic Acid into Diphenylsuccino*-p-*tolil.*

A. *By the Action of Ethyl-alcoholic Hydrogen Chloride.*—The acid (1·8 grams) was heated under reflux with ethyl-alcoholic hydrogen chloride solution (8 per cent.; 10 c.c.). A homogeneous solution was readily obtained, from which a precipitate separated after a few minutes. The solvent was removed on the water-bath and the residue purified by crystallisation from much alcohol.

Diphenylsuccino-p-*tolil* separates from boiling ethyl alcohol in long, slender needles which, although apparently perfectly stable when dry, frequently crumble to microscopic prisms when preserved beneath the mother liquor. It dissolves sparingly in the boiling, very sparingly in the cold solvent; it is readily soluble in cold acetone, moderately so in cold chloroform or benzene, and sparingly so in cold ether. It melts at 170°:

0·1739 gave 0·5182 CO_2 and 0·0884 H_2O. C = 81·3; H = 5·7.
$C_{23}H_{19}O_2N$ requires C = 80·9; H = 5·6 per cent.

B. *By the Action of Heat.*—The *r*-acid was heated in a small tube at 195—205° during fifteen minutes, at the end of which period the evolution of gas had ceased. The residue was crystallised from alcohol, from which it separated in slender needles which disintegrated to microscopic prisms. It melted at 170°, and was thus identified as diphenylsuccino-*p*-tolil.

The behaviour of *r*-diphenylsuccino-*p*-toluidic acid is thus very similar to that of the corresponding anilic acid; it is, however, curious that the melting point of the tolil is lower than that of the toluidic acid, whilst the reverse is the case with the aniline derivatives.

*Action of Alkali on Diphenylsuccino-*p*-tolil.*

Diphenylsuccino-*p*-tolil (5 grams) was boiled during forty-five minutes with aqueous-alcoholic sodium hydroxide solution (1·2*N*; 40 c.c. Water : alcohol : : 1 : 3). The sodium salts thus formed were converted into the barium derivatives, which were separated by treatment with water. From the less readily soluble salt, *r*-diphenylsuccino-*p*-toluidic acid, melting at 194—195°, was easily isolated; the more readily soluble portion yielded, on acidification, crude *meso*diphenylsuccino-*p*-toluidic acid, which was purified by crystallisation from slightly diluted acetic acid.

meso*Diphenylsuccino-*p*-toluidic acid* separates from alcohol or dilute acetic acid in minute, colourless needles which melt and decompose slightly at 206°. It is moderately soluble in cold methyl or ethyl alcohol or in acetic acid, sparingly so in water or hot benzene, readily so in ether or acetone, and practically insoluble in light petroleum or carbon tetrachloride. When heated at 215° during five minutes or boiled with ethyl-alcoholic hydrogen chloride, it is transformed into diphenylsuccino-*p*-tolil:

0·1216 neutralised 3·4 c.c. of *N*/10-sodium hydroxide. Calc.: 3·39 c.c.

0·1457 gave 0·4128 CO_2 and 0·0804 H_2O. C = 77·25; H = 6·13.
$C_{23}H_{21}O_3N$ requires C = 76·88; H = 5·85 per cent.

The authors desire to express their gratitude to the Research Fund Committee of the Royal Society for a grant which has defrayed a part of the expense of the investigation.

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BELFAST. [*Received, September 9th,* 1918.]

LXXVII.—*The Inflammation of Mixtures of Methane and Air in a Closed Vessel.*

By RICHARD VERNON WHEELER.

WHEN an inflammable mixture of gas and air is ignited within an inflexible closed space, flame travels throughout the mixture in a manner and at a speed dependent mainly on the nature and proportion of the inflammable gas present. The manner in which the flame spreads through the mixture is affected also by the shape

of the containing vessel and the position of the point of ignition, and the speed of the flame is affected by these factors as well as by the intensity of the means of ignition and the initial temperature and pressure of the mixture. To such causes of variation in the manner and speed of the spreading of flame must be added mechanical agitation or turbulence of the mixture, such as is induced, for example, within a gas-engine cylinder during the introduction of the charge (see Dugald Clerk, "The working fluid of internal-combustion engines," Gustave Ganet Lecture, Junior Institution of Engineers, 1913).

The inflammation of the mixture within the closed vessel, inasmuch as it results in the formation of products of combustion at a high temperature, causes an increase of pressure. If the vessel were impervious to heat, the maximum pressure developed would afford a measure of the thermal energy of the products of combustion, which should be equal to the chemical energy of the uninflamed mixture.

The present paper records the results of a study of the inflammation of different mixtures of pure methane and air in closed spherical vessels. The principal data obtained were: (1) the maximum pressures developed, (2) the rates of development of pressure, and (3) the speeds of propagation of flame. Details as to the manner in which these data were obtained, and of the precautions taken to ensure their accuracy, are given in the experimental portion of the paper.

Development of Pressure.

In the table that follows are given the maximum pressures developed by different mixtures of methane and air when ignited within spherical vessels of about (*a*) 4 litres and (*b*) 16 litres capacity, 19·5 and 31·2 cm. in diameter, respectively. For comparison, Mallard and Le Chatelier's determinations (*Ann. des Mines*, 1883, [viii], **4**, 379), for which they used a cylindrical vessel 17 cm. long and 17 cm. in diameter, are included in the table on p. 842.

These results are shown graphically in Fig. 1. It is of importance to notice that the maximum pressures for similar mixtures in the 4-litre and the 16-litre spheres, as determined by interpolation, are practically identical.

The values quoted as Mallard and Le Chatelier's are their observed values (*loc. cit.*, p. 509). They are rather irregular and are considerably higher than the results obtained for similar mixtures in the spheres. This may be due to impurity of the com-

Methane in mixture. Per cent. by volume.	Maximum recorded pressures above atmospheric. Atmospheres. 4-Litre sphere.	16-Litre sphere.	3·86-Litre cylinder (Mallard and Le Chatelier).
6·05	—	2·86	—
6·30	3·20	—	—
6·80	5·10	—	5·51
6·85	—	4·35	—
7·45	5·64	—	—
7·80	—	5·85	—
7·95	6·09	—	—
8·00	—	—	6·53
8·45	6·40	—	—
8·80	—	6·66	—
9·20	6·73	—	7·41
9·40	6·80	—	—
9·50	—	—	7·75
9·65	6·90	—	—
9·80	—	6·94	7·55
10·00	—	—	7·34
10·10	6·97	—	—
10·25	6·97	—	—
10·60	—	—	7·48
10·75	6·87	—	—
10·80	—	6·80	—
11·20	—	—	6·94
11·40	6·73	—	—
11·90	—	6·40	—
12·10	6·36	—	—
12·50	—	—	6·46
12·80	—	5·78	—
12·90	5·78	—	—
13·40	4·80	—	—
13·90	3·54	—	—

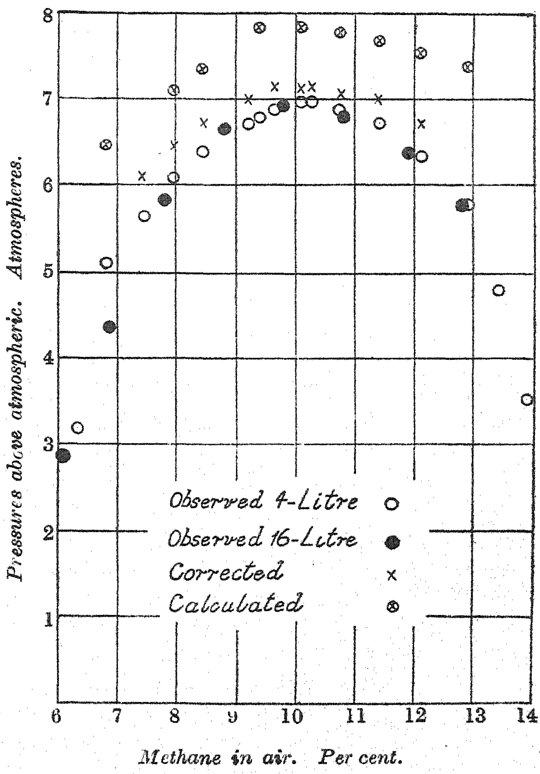
bustible gas used, regarding which the fact is recorded (*loc. cit.*, p. 409) that it contained some gas richer in carbon than methane. The gas was prepared from sodium acetate, and would contain ethylene and acetone vapour.

Reference should be made also to some experiments by Beyling (*Glückauf*, 1906, **42**, 130), who used a cylindrical vessel of 42 litres capacity, 33·5 cm. in diameter and 42·5 cm. long. The maximum pressure recorded as produced by any mixture of methane and air was 6·5 atmospheres. In a vessel of smaller capacity (about 11 litres) the maximum pressure was the same.

By reason of the shape of their explosion-vessel, Mallard and Le Chatelier found it necessary to introduce a correction for cooling during the propagation of flame, averaging about 10 per cent. on their observed pressures. If ignition of an inflammable mixture is exactly at the centre of a perfectly spherical vessel, it is probable that the propagation of flame follows regular concentric spherical surfaces in such a manner that the flame reaches the

walls of the vessel simultaneously at all points; for, except with very slowly moving flames, or, possibly, in very large vessels, it is unlikely that convection currents will have time materially to affect the speed in any particular direction. The whole of the mixture is thus inflamed before cooling by conduction of heat by the walls of the vessel can come into play.*

FIG 1.



If, however, the vessel is not perfectly spherical, or if ignition is not truly central, flame will touch the walls sooner at some places than at others, and cooling of the products of combustion will begin before propagation of flame is complete. The maximum

* Cooling by the walls, before the whole mixture is inflamed, may cause a negligible loss of heat if the unburnt mixture in contact with them is heated by compression (due to dilation of the burnt mixture at the centre of the vessel) before flame reaches it.

pressure within the vessel as recorded by a gauge is not then that which the mixture would exert were the whole brought at once to the temperature of combustion. The fact that Mallard and Le Chatelier used a cylinder for their experiments, although they ignited the mixture at the centre, caused the propagation of flame within the vessel to assume two phases. During the first phase the flame travelled from the centre as, presumably, a spherical envelope until it touched the walls of the vessel (the height of which was equal to the diameter). The second phase then began and continued until the flame reached the curve of intersection of the ends with the cylindrical walls, when inflammation was complete. Throughout this second phase, cooling of the products of combustion by the walls took place, the amount of cooling increasing with the progress of the flame, since the area of the surface of the cylinder in contact with the heated gases increased.

A correction to be added to Mallard and Le Chatelier's recorded figures for maximum pressures is, on this reasoning, necessary. The correction when applied brings the pressures developed by all their mixtures of "methane" and air from one to one and a third atmospheres higher than the pressures recorded in the spherical vessels. The question then arises whether a similar correction should not also be applied to the latter results—whether, in fact, one is justified in assuming that with central ignition in a spherical vessel flame spreads at the same speed in all directions. Langen ("Mitteillungen u. Forschungsarbeiten aus dem Gebeite des Ingenieurwesens," vol. 8, 1903), who used a spherical vessel for similar experiments, did, indeed, introduce a "cooling correction." This, however, was on account of a short neck, at the top of the sphere, to which the pressure-gauge was attached; Langen assumed that throughout the spherical portion of his vessel the flame in any given mixture spread in all directions at the same speed.

In order to test the truth of this supposition, a series of measurements was made of the intervals of time that elapsed between ignition and the advent of flame at the top and bottom of a closed vessel filled with different mixtures of methane and air. With all mixtures containing more than 7·5 and less than 12·5 per cent. of methane, the time-intervals for upward and for downward propagation of flame were identical. They coincided also for each mixture with the time that elapsed between ignition and the attainment of maximum pressure in a vessel of the same dimensions. With mixtures containing less than 7·5 and more than 12·5 per cent. of methane, in which the rate of propagation of flame is slow, flame reached the bottom of the vessel later than it reached the top by an amount of time which varied with the methane-con-

tent of the mixture. Thus the measurements for three mixtures were:

Methane in mixture. Per cent.	Time required for the flame to travel 9·75 cm. from the point of ignition. Upwards.	Downwards.
6·40	0·260 sec.	0·468 sec.
6·95	0·169 ,,	0·234 ,,
13·00	0·219 ,,	0·320 ,,

With such mixtures, therefore, cooling of the products of combustion takes place before the attainment of the maximum recorded pressure, even in a spherical vessel, by reason of the contact of the upper part of the flame with the walls of the vessel before the lower part of the mixture is burnt.

It should be noted that the limits of inflammability of methane–air mixtures ignited at the centre of a closed spherical vessel are 5·6 per cent. lower and 14·8 per cent. upper (T., 1911, **99**, 2013). The progress of the flame in these mixtures is sufficiently slow to follow by the eye; the flame travels upwards from the spark as an inverted cone, fills the upper third of the vessel, and thence travels slowly downwards as a horizontal disk to the bottom.

With the mixtures containing more than 7·5 and less than 12·5 per cent. of methane, however, no loss of heat through cooling by the walls before the whole of the mixture has been inflamed should arise in a spherical vessel, other than the negligible quantity transmitted by the layer in contact with the walls during the interval of time that elapses between its compression by the inflamed core (and consequent heating) and its burning. Over this range, then, no such correction for cooling as Mallard and Le Chatelier and Langen applied is required when perfectly spherical vessels are used and ignition is at the centre. One would arrive at the same conclusion from the fact, already noted, that the maximum pressures recorded were the same, within 1 per cent., over the range 7·5 to 12·5 per cent. of methane, in the 4-litre as in the 16-litre sphere, although the ratio surface/volume was 1·6 times as great with the former as with the latter.

Experiment thus shows that one is justified in assuming, over the major portion of the range of inflammable mixtures of methane and air, no loss of heat in a spherical vessel due to contact of part of the flame with the walls before the whole of the mixture is burnt. Yet one cannot assume that the maximum recorded pressure in such a vessel gives a measure of the internal energy of the products of combustion, which should be equal to the chemical energy of the uninflamed mixture, or, in other words,

that the pressure recorded is that which would be attained were the vessel impervious to heat.

Apart from loss by radiation during the propagation of flame, it must be remembered that at the moment when the vessel is just filled with flame (that is, at the moment of maximum recorded pressure in a spherical vessel), the products of combustion are not in thermal equilibrium (see, in this connexion, the First Report [1910] of the Committee, appointed by the British Association, for the investigation of gaseous explosions). Hopkinson, *Proc. Roy. Soc.*, 1906, [*A*], **77**, 387) has shown that at the moment of maximum pressure of a mixture of coal gas and air, the temperature around the point of ignition at the centre of a cylindrical vessel was several hundred degrees higher than the mean temperature (as deduced from the pressure), owing to adiabatic compression of the products of combustion there during the burning of the remainder of the mixture; whilst at the sides and ends of the vessel, where the gases were compressed before ignition, the temperature reached was as much below the mean.

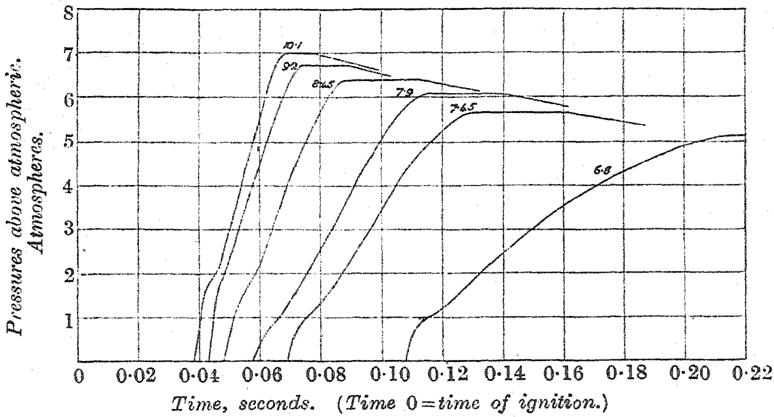
If the volumetric heats of the gases comprising the products of combustion were constant at all temperatures, the attainment of a uniform temperature within a closed vessel by convection and conduction would cause no alteration in pressure; but inasmuch as the volumetric heats are not constant, being perhaps half as great again in the hottest as in the coldest part of the gaseous mass, the attainment of thermal equilibrium should be attended by a change of pressure.

During the time that thermal equilibrium is being established, after complete inflammation has taken place, the cold walls of the spherical containing vessel are everywhere in contact with hot gases, so that simultaneously with any increase in pressure that might result from the equalisation of the temperature differences within the gaseous mass, there is a reduction of pressure due to loss of heat by conduction. This loss, and radiation losses during the same period as well as during the propagation of flame, combine to render the recorded pressures lower than those representative of the chemical energy of the uninflamed mixtures. It is difficult to make even a rough calculation of the change of pressure that should occur owing to the establishment of thermal equilibrium, because of lack of knowledge of the distribution of temperature within a spherical vessel at the moment of complete inflammation. It is possible, however, if certain assumptions are made, to obtain some idea of the order of magnitude of the pressure change from an examination of the time–pressure diagrams.

Diagrams for representative mixtures used in the 4-litre sphere

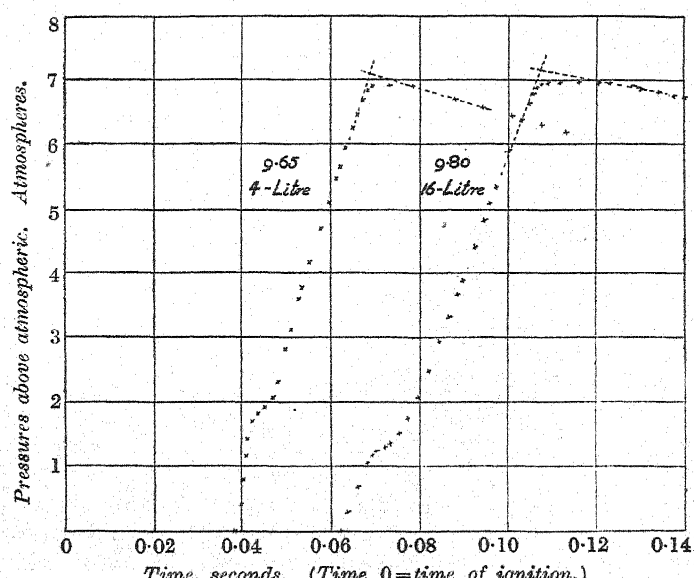
are shown in Fig. 2, whilst in Fig. 3 are given the diagrams for mixtures of nearly the same methane-content, the one (9·65 per

FIG. 2.



cent. methane) in the 4-litre and the other (9·80 per cent. methane) in the 16-litre sphere. These diagrams are reproduced on a

FIG. 3.



different scale from the actual records of the indicator in the manner described in the experimental portion of this paper.

Examination of these curves shows that each exhibits three stages of development. During the first stage the pressure increases proportionately with the time, during the second it remains constant, and during the third it gradually decreases.

The first stage, during which the pressure increases, corresponds with the propagation of flame within the sphere; as will be shown later, the maximum pressure for all mixtures containing between 7·5 and 12·5 per cent. of methane is attained simultaneously with the advent of flame at the boundary of the mixture. For mixtures containing less than 7·5 or more than 12·5 per cent. of methane, the attainment of maximum pressure synchronises with the advent of flame at the top of the vessel.

The last stage, the beginning only of which is shown in each diagram, represents the cooling of the products of combustion.

The second stage, during which the recorded pressure remains constant, may represent any or all of three possibilities: (1) The occurrence of successive stages in the combustion of methane, the mechanism of which can be represented by the equation

$$CH_4 + O_2 = (CH_2O + H_2O) = CO + H_2 + H_2O,$$

with subsequent burning of the carbon monoxide and hydrogen if oxygen is in excess; (2) exothermic secondary reaction between carbon monoxide and steam (compare Bone, *Phil. Trans.*, 1915, [*A*], **215**, 318); or (3) the equalisation of temperature differences within the gaseous mass, with consequent increase of pressure due to change in the volumetric heats of the products of combustion.

The duration of the period of constant pressure varies with the composition of the mixture of methane and air, the time intervals being:

Methane, per cent.	Duration of period of constant pressure.
7·45	0·031 sec.
7·95	0·026 ,,
8·45	0·024 ,,
9·20	0·016 ,,
9·40	0·010 ,,
9·65	0·009 ,,
10·10	0·010 ,,
10·25	0·009 ,,
10·75	0·013 ,,
11·40	0·018 ,,
12·10	0·024 ,,

These figures are not consistent with either of the suppositions (1) and (2) given above; for if stages in the combustion of methane are indicated by the period of constant pressure, one would expect that period to be shorter the greater the excess of oxygen present in the mixture, whilst the occurrence of the exothermic secondary reaction between carbon monoxide and steam should be most pro-

nounced when there is excess of methane above that required for complete combustion to carbon dioxide and steam.

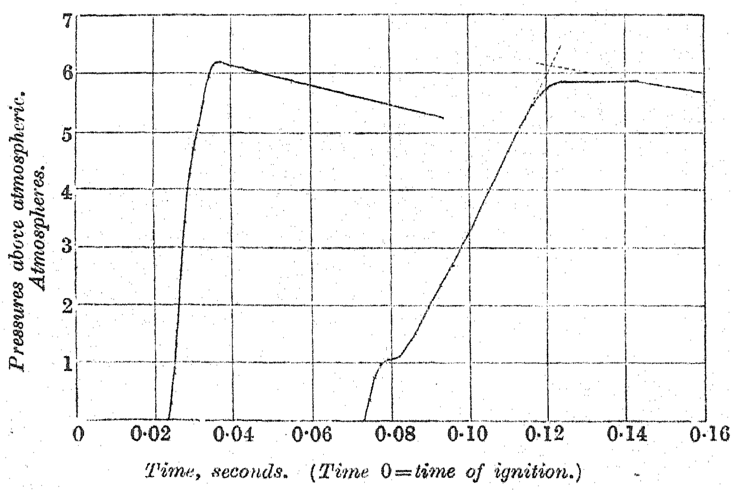
On the other hand, the figures support the view that the change of volumetric heats of the gases during the attainment of thermal equilibrium is responsible for an increase of pressure balancing a decrease due to cooling; for the duration of the period of constant pressure is shorter the higher the pressure attained, that is to say, the higher the mean temperature of the products of combustion. Moreover, reference to Fig. 3 shows that the period of constant pressure for mixtures of about the same methane-content was nearly twice as long in the 16-litre as in the 4-litre sphere.

Let us, then, assume that the second stage in the time–pressure diagrams represents a balance between a gradual decrease of pressure that begins as soon as inflammation of the mixture is complete and is due to cooling by the walls of the vessel, and an increase of pressure incident at the same moment and due to the gradual attainment of thermal equilibrium. Mallard and Le Chatelier have shown (*loc. cit.*, p. 454, and Plate XIV, Fig. 8) that the cooling curve for the products of combustion of methane and air is a straight line. It is therefore permissible to extend the cooling curves of the time–pressure diagrams backwards, as shown in Fig. 3. The portion of each curve representing the propagation of flame within the vessel is, after the initial impetus to the flame given by the source of ignition has died down, also nearly a straight line, although there is a slight diminution in the rate of development of pressure just before the maximum is reached. A line drawn extending the straight portion of this curve so as to cut the prolongation of the cooling curve should give, within a close approximation, the pressure that would be attained after the complete inflammation of the mixture did no cooling take place. This has been done for the two curves in Fig. 3, from which it will be seen that the "correction" amounts to, at most, 3 per cent.

The validity of the assumption that such a correction can and should be applied might be tested if means could be employed to ensure a rapid equalisation of the temperature differences within the vessel at the moment of complete inflammation. Experiments made in the course of another investigation (see "Third Report of the Explosions in Mines Committee," p. 26, London, 1913), during which a small fan was rapidly revolved within the sphere, may serve to illustrate the effect of aiding convection currents. The fan had four helical blades and was run at the rate of 100 revolutions per second. The results of a pair of experiments, one with and the other without the fan, using a mixture of ethane and air

containing 4·05 per cent. of ethane, are shown in Fig. 4. The maximum pressure recorded when the fan was revolving was higher than when the mixture was at rest by 0·23 atmosphere, an amount a little more (0·07 atmosphere) than the "correction" obtained in the manner described. This diagram illustrates also the effect of turbulence of the mixture on the speed of inflammation, an effect already noted by Dugald Clerk and Hopkinson. With the fan running, the time taken, measured from the moment of ignition, for the attainment of maximum pressure was 0·0362 sec.; without the fan, it was 0·1244 sec. No doubt the higher pressure reached in the former experiment was in part due to smaller radiation loss during the more rapid propagation of flame.

FIG. 4.



Whatever the cause of evolution of heat, the horizontal portion of the time–pressure diagram represents a balance between heat evolved after flame has travelled throughout the mixture and heat dissipated, and the correction to be applied on this score cannot exceed the quantity deduced by extrapolation of the cooling and propagation curves. In Fig. 1 are shown the "corrected" pressures for mixtures over the range 7·5 to 12·5 per cent. of methane, together with the calculated maximum pressures those mixtures should produce, taking Langen's values for the specific heats of the various gases and assuming no loss of heat by radiation.

The calculated values are about 10 per cent. greater than the observed over the whole range. This difference, assuming the

correctness of the values taken for the specific heats of the gases, must be due mainly to loss of heat by radiation during the propagation of flame in the spheres, for it has been shown that up to the time of attainment of maximum pressure flame does not touch the walls of the vessels.* For information regarding the probable loss of heat by radiation, only the results of Hopkinson (*Proc. Roy. Soc.*, 1911, [*A*], **84**, 155) with mixtures of coal-gas and air, and of David (*Phil. Trans.*, 1912, [*A*], **211**, 375) with coal-gas–air and hydrogen–air mixtures are available, and direct comparison of these with methane–air mixtures cannot be made.

It has been shown, however (David), that up to the time of maximum pressure (attained in 0·05 sec.), a 15 per cent. coal-gas–air mixture radiated about 3 per cent. of its total heat of combustion, the maximum temperature reached being 2400° abs. A 25·4 per cent. hydrogen–air mixture, which developed the same maximum temperature, radiated about 0·5 per cent. only of its total heat of combustion up to the time of attainment of maximum pressure (in 0·017 sec.). The coal-gas used probably contained about 50 per cent. of hydrogen and 35 per cent. of methane (and other hydrocarbons); it is known that the radiation from the mixtures is due almost entirely to the steam and carbon dioxide that they contain, and that carbon dioxide has a radiating power about 2·4 times that of an equal volume of steam (R. von Helmholtz, "Die Licht- und Warmestrahlungverbrennender Gase," Berlin, 1890); an estimated loss due to radiation of about 10 per cent. of the total heat of combustion during the propagation of flame in the mixtures of methane and air may therefore be not far from the truth.

Propagation of Flame.

Each of the time–pressure diagrams shown in Figs. 2 to 4 has been plotted with the time of passage of the secondary discharge that caused the ignition of the mixture as zero time. It has been assumed by the majority of experimenters on the inflammation of gaseous mixtures in closed vessels that the time of ignition synchronises with the time of first manifestation of pressure on the indicator or gauge. Bairstow and Alexander (*Proc. Roy. Soc.*, 1905, [*A*], **76**, 340) found, however, that this was not so in their experiments with mixtures of coal-gas and air; and it is apparent from the diagrams for methane–air mixtures given in this paper that there is a definite interval of time, the length of which depends on the composition of the mixture, between the ignition

* A slight amount of cooling no doubt arises through conduction of heat by the electrodes.

of the mixture at the centre of a spherical vessel and the first appearance of pressure on an indicator fixed at the top.

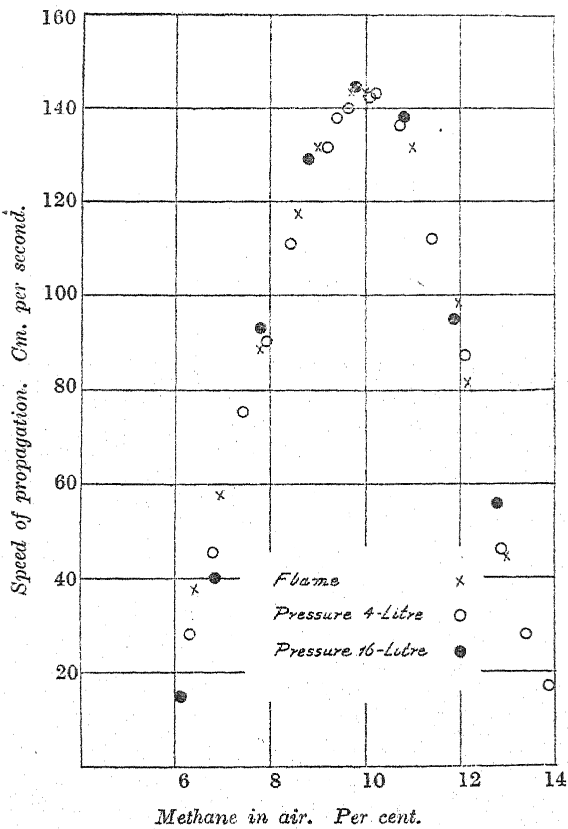
In order to be able to trace the progress of the flame within the vessels from the time–pressure diagrams, records were taken of the time that elapsed between the passage of an electric spark at the centre of a closed vessel containing different mixtures of methane and air and the appearance of flame at a point 7·5 cm. vertically upwards, in the manner described in the experimental portion of this paper. The time-intervals calculated for a distance of 9·75 cm. were found to correspond closely with the times taken for the development of the maximum pressures in similar mixtures in the 4-litre sphere (radius, 9·75 cm.), as the following table

		4-Litre sphere.		16-Litre sphere.		
Methane in mixture. Per cent.	Time taken for flame to travel 9·75 cm. upwards. Seconds.	Time between ignition and first appearance of pressure. Seconds.	Time between ignition and attainment of maximum pressure. Seconds.	Time between ignition and first appearance of pressure. Seconds.	Time between ignition and attainment of maximum pressure. Seconds.	Mean speed of flame. Cm. per sec.
6·05	—	—	—	0·4233	1·0370	15
6·30	—	0·1800	0·3484	—	—	28
6·40	0·260	—	—	—	—	37·5
6·80	—	0·1080	0·2150	—	—	45·5
6·85	—	—	—	0·1830	0·3877	40
6·95	0·169	—	—	—	—	58
7·45	—	0·0690	0·1302	—	—	75
7·80	0·110	—	—	0·1021	0·1680	89, 93
7·95	—	0·0574	0·1084	—	—	90
8·45	—	0·0484	0·0878	—	—	111
8·60	0·083	—	—	—	—	117·5
8·80	—	—	—	0·0713	0·1206	129
9·00	0·074	—	—	—	—	132
9·20	—	0·0428	0·0720	—	—	132
9·40	—	0·0392	0·0707	—	—	138
9·65	—	0·0382	0·0696	—	—	140
9·70	0·068	—	—	—	—	143·5
9·80	—	—	—	0·0623	0·1080	144·5
10·00	0·068	—	—	—	—	143·5
10·10	—	0·0383	0·0684	—	—	142·5
10·25	—	0·0382	0·0682	—	—	143
10·75	—	0·0395	0·0715	—	—	136
10·80	—	—	—	0·0665	0·1130	138
11·00	0·074	—	—	—	—	132
11·40	—	0·0498	0·0870	—	—	112
11·90	—	—	—	0·1000	0·1640	95
12·00	0·099	—	—	—	—	98·5
12·10	—	0·0694	0·1164	—	—	87
12·20	0·120	—	—	—	—	81
12·80	—	—	—	0·1320	0·2800	56
12·90	—	0·1150	0·2120	—	—	46
13·00	0·219	—	—	—	—	44·5
13·40	—	0·1600	0·3470	—	—	28
13·90	—	0·2150	0·5700	—	—	17

shows. In the same table are given the time-intervals between ignition and the attainment of maximum pressure in the 16-litre sphere (radius, 15·6 cm.) and the calculated mean speeds of the flames in cm. per second.

The correspondence between the time taken for flame to travel from the centre to the top in the spheres and the time taken for

FIG. 5.



the attainment of the maximum pressures is perhaps best shown in Fig. 5, where the mean speeds of the flames, in cm. per sec., are plotted against percentages of methane in the mixtures, different symbols being used according as the points on the curve are (1) actual determinations of the rate of travel of flame, (2) calculated from the time-interval between ignition and the attainment of maximum pressure in the 4-litre sphere, or (3) calcu-

lated from the time-interval between ignition and the attainment of maximum pressure in the 16-litre sphere.

It is of interest to compare these speeds with the speeds during the "uniform movement" of flame in similar mixtures (see T., 1917, **111**, 1044), although the conditions under which propagation takes place are different. The shapes of the speed–percentage curves for the two modes of propagation are similar, the speeds in each exhibiting maxima over the range 9·5 to 10·5 per cent. methane and decreasing regularly on either side of this range. The speeds are, moreover, of the same order of magnitude (compare, for example, the speeds during the uniform movement of flame in a tube 30·5 cm. in diameter), in which connexion it may be noted that the high speeds recorded by Mallard and Le Chatelier for the propagation of flame in mixtures of methane and air in a closed cylinder (*loc. cit.*, p. 464) are due to those authors regarding the first indications of pressure on their time–pressure diagrams as coincident with the times of ignition of the mixtures.

If it is assumed, for the sake of calculation, that the flames in the spheres travelled at the observed mean speeds from the point of ignition, it is found that in the 4-litre sphere no pressure was indicated until the flame had travelled from 5 to 5·5 cm. (the calculated distance is remarkably constant over the whole range of mixtures), whilst in the 16-litre sphere flame travelled from 9 to 10 cm. before any pressure was indicated. That is to say, over the range 7·5 to 12·5 per cent. of methane, where the flame is propagated in all directions at the same speed, about one-fifth of the mixture had been inflamed in each vessel before any indication of pressure was obtained.

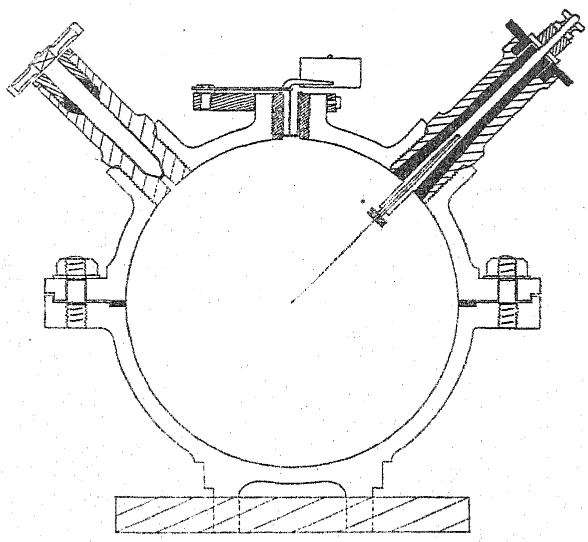
EXPERIMENTAL.

The Measurement of Pressure.—The spheres, 19·5 and 31·2 cm. in diameter respectively, were machined castings of bronze. A section of one of them—both were of the same design—is shown in Fig. 6. The sphere is cast in two halves bolted together with a loose ring of copper as washer. It is pierced at the top by a hole carrying a fixed sleeve of hardened steel, highly polished, the internal diameter of which is 12·75 mm. A hollow piston of hardened steel is ground and polished to fit the sleeve; the surface of the piston on which the pressure within the vessel acts is 78·5 sq. mm., the piston being prevented from passing through the sleeve by a thin ring of steel at the base thereof. Other fittings are: (*a*) a valve for exhaustion and the introduction of the inflammable mixture, (*b*) insulated electrodes reaching to the centre,

(*c*) a small window of quartz, and (*d*) a removable shaft carrying a small broad-bladed fan. The last-named was removed during all the experiments described in this paper, save the one wherein the use of the fan is specified. The fittings on the sphere for the piston, valve, and quartz window are flush with the inner surface, which is highly polished. Both spheres were made by Mr. C. W. Cook, of the University Engineering Works, Manchester.

The manometer is a triangular plate of tempered steel 2·6 mm. in thickness, the base of which is clamped, the apex making contact with the hollow piston in the sphere by means of a loose rod of steel, the lower end of which rests in a conical depression at the

FIG. 6.



centre of the base of the piston, whilst the upper end rests in a similar depression in the spring. A thin strip of steel is attached to the apex of the spring and carries a scribing style, which rests lightly against the surface of a smoked paper band on a drum revolved by an electric motor.

With this form of spring, the maximum strain is the same at all cross-sections, and the inertia is small, since it is the narrow part of the spring which moves most and the wide part least. The deflexion of the scribing style, equivalent to a pressure of one atmosphere, applied to the piston is 1·38 mm. The period of the indicator is 1/250-sec.

The graphs produced by the scribing style on the smoked-paper chart (which receives also a record of the time of passage of the secondary discharge spark used to ignite the mixtures and the trace of an electrically driven tuning-fork making fifty vibrations per second) are measured, after fixation of the chart in a bath of weak spirit varnish, by the aid of a specially designed apparatus (see "Record of First Series of the British Coal Dust Experiments," p. 75, London, 1910), consisting essentially of a microscope with fine cross-wires in the eyepiece and a drum mounted on V-supports in which it can rotate or slide laterally. The circumference of the drum is divided into millimetres and rests against a vernier, whilst lateral movement of the drum is measured by means of a micrometer screw with a divided head.

Method of Conducting an Experiment.—The sphere having been assembled, it was exhausted of air to within a few mm. of mercury by means of a Gaede mercury pump, and the mixture to be experimented with introduced. Each mixture was prepared in an 18-litre glass gas-holder over glycerol and water, well shaken, and allowed to remain during six hours, and analysed before use. The secondary discharge used to ignite the mixtures was obtained from a "10-inch" X-ray coil by breaking a current of 10 amperes in the primary circuit, the trembler being locked. The discharge passed across a 10 mm. gap at the centre of the sphere, and simultaneously a record of its passage was made on the smoked-paper chart on the revolving drum.

Speed of Propagation of Flame.—Measurements of the speeds of propagation of flame were obtained for a series of mixtures by recording the time of passage of the secondary discharge used to ignite them at the centre of the vessel and the time at which short screen wires of copper 0·025 mm. in diameter, stretched at a distance of 7·5 cm. vertically above and below the point of ignition, were melted. The screen wires carried an electric current of 0·5 ampere at 4 volts and were in series with the electromagnets of delicate Deprez indicators, the latency or "time-lag" of which was found to be negligible. (The armatures, carrying aluminium styles for recording on the smoked-paper chart, moved freely with a current of 0·1 ampere at 1 volt.)

Calculation of Theoretical Maximum Pressures.—For the purpose of calculating the theoretical maximum pressures that should be given by the different mixtures, it was necessary to obtain information as to the proportion of the methane completely burned to form carbon dioxide and steam at the time of attainment of maximum pressure, more particularly in those mixtures containing excess of methane. To this end, a series of experiments was made

in which a capillary tube of copper, fitted with a tap, was fixed through the side of the 4-litre sphere (in place of the quartz window). The tube projected 4·8 cm. within the sphere (that is, midway between the centre and the circumference), and outside the sphere, beyond the tap, it was bent so as to dip below the surface of mercury in a trough. A gas-collecting tube of 25 c.c. capacity, filled with mercury, was inverted in the trough over the end of the bent tube.

The sphere was filled with the inflammable mixture in the usual manner, enough gas passed through the copper delivery tube to displace the air therein, and the tap closed. The mixture having been ignited, the tap was opened at the moment of attainment of maximum pressure by revolving it rapidly through 180 degrees. During the short time that the tap was thus opened, the pressure within the sphere forced out into the collecting tube between 5 and 10 c.c. of the products of combustion, a quantity sufficient for accurate analysis.

The results of the analyses, after making a correction for the unburnt mixture contained in the capillary tube, were as follow:

Methane in original mixture.	Analysis of products of combustion.				
Per cent.	CO_2.	O_2.	CO.	H_2.	CH_4.
7·90	9·25	3·82	0·15	nil	nil
9·40	11·14	0·74	0·26	nil	nil
9·90	10·66	0·13	1·12	0·40	0·24
10·00	10·86	0·04	1·08	0·68	0·04
10·70	9·04	nil	3·63	2·21	0·10
11·05	9·00	nil	3·44	1·95	0·23
12·10	8·09	0·07	5·85	4·00	0·07
12·90	6·08	0·05	7·78	6·73	0·36
13·90	5·45	nil	8·95	9·45	1·00
14·70	4·13	nil	9·85	11·15	0·61

These results should be compared with similar analyses of "flame gases" obtained during the propagation of flame in upper limit mixtures with air and with mixtures of oxygen and nitrogen containing less oxygen than air (T., 1914, **105**, 2596). The percentages of the total methane in the original mixtures burnt to form carbon dioxide and steam are plotted against the ratios O_2/CH_4 in the original mixtures in Fig. 7, which includes also the results obtained with the upper limit mixtures. From the curve so obtained, it is possible to estimate for any mixture of methane and air, with sufficient accuracy for the calculation of the heat developed, the proportions in which the reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 191{,}070 \text{ calories} \quad . \quad . \quad . \quad . \quad (1)$$
$$CH_4 + O_2 = CO + H_2 + H_2O + 65{,}760 \text{ calories} \quad . \quad . \quad . \quad . \quad (2)$$

can be assumed to have taken place during combustion.

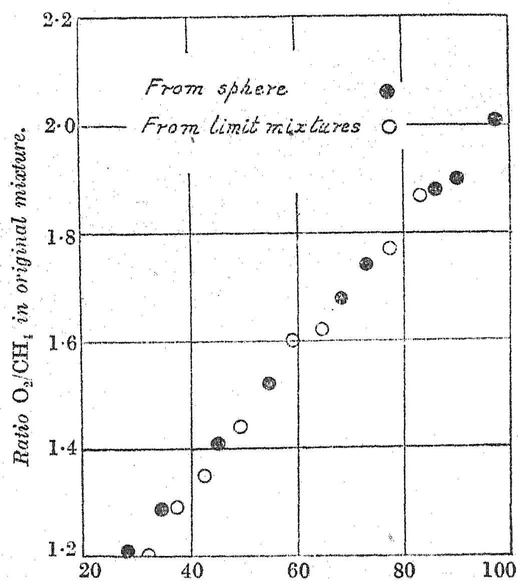
The calculation is as follows. The mixtures being saturated with water vapour at 15°, the original pressure of the mixture is 0·983 atmosphere, with 0·017 atmosphere of water vapour. The final pressure, if the gases are cooled to 15° without condensation of steam, is equal to the original pressure plus the partial pressure of any methane burnt according to equation (2).

Let Q be the heat of the reaction, then

$$Q = pCH_4(aq + bq'),$$

where pCH_4 is the partial pressure of the methane burnt (corrected

FIG. 7.



Percentage of methane burnt appearing as CO_2 and steam.

for the presence of water vapour), a and b represent the proportions burnt according to equations (1) and (2) respectively, and q and q' the corresponding heats of combustion.

The rise of temperature, t, is given by the equation

$$t = \frac{pCH_4(aq+bq')}{(pH_2+pO_2+pN_2+pCO)(4{\cdot}8+0{\cdot}0006t)+pCO_2(6{\cdot}7+0{\cdot}0026t)+pH_2O(5{\cdot}9+0{\cdot}00215t)}.$$

Where unburnt methane remains in the mixture a term for the specific heat of methane, appropriate to the temperature, requires to be introduced in the denominator on the right-hand side of the equation.

The absolute pressure, P, is given, in atmospheres, by the equation

$$P = \frac{t+288}{288}(p + pCH_4 \, . \, b).$$

The majority of the experiments described in this paper were carried out during the winter of 1912 with the assistance of Mr. M. J. Burgess. For the experiments on the speeds of propagation of flame, as well as for assistance in checking some of the earlier results, I am indebted to Mr. W. Mason.

ESKMEALS,
CUMBERLAND. [*Received, August 12th*, 1918.]

LXXVIII.—*A Synthesis of* iso*Brazilein and Certain Related Anhydropyranol Salts. Part I.**

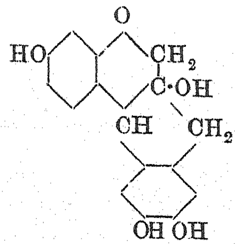
By HERBERT GRACE CRABTREE and ROBERT ROBINSON.

ALTHOUGH accumulated evidence decisively establishes the constitution of brazilin, it must be admitted that the necessary arguments are somewhat intricate, and consequently the problem of the synthesis † of the substance and its more important derivatives

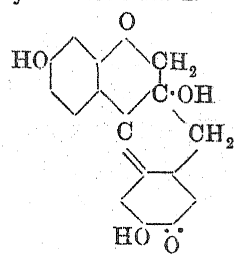
* The original intention of the authors to publish this research as a single communication has been revised in view of the very considerable delay which has been caused by their inability to complete the experimental work under existing conditions. They have reserved for Part II. a description of the homologues of the methylated *iso*brazilein salts, and also the intermediate product in the synthesis and the identification of the synthesised *iso*brazilein with that obtained from brazilin. It is hoped that the method of synthesis of *iso*brazilein may prove applicable also to the synthesis of *iso*hæmatein.

† Pfeiffer and Grimmer in a communication (*Ber.*, 1917, **50**, 911) bearing the rather misleading title, "The Brazilin Question," have announced their intention of attacking the problem of the synthesis of brazilin and its derivatives, but are apparently unaware that the method they propose to employ has already been indicated by Perkin and Robinson (P., 1912, **28**, 7). The former authors have so far obtained 3-anisylidene-7-methoxy-2 : 3-dihydro-1 : 4-benzopyrone, whereas the latter prepared a nearer relative of brazilin, namely, 3-veratrylidene-7-methoxy-2 : 3-dihydro-1 : 4-benzopyrone, and stated that they had made observations indicating the probability that the substance could be converted into a derivative of brazilin. This veratrylidene compound was later prepared in larger amount and in a purer condition, and the research was elaborated in various directions, although a number of circumstances have combined to retard the completion of the work. There has, however, never been any intention of abandoning a line of investigation which has always been regarded as likely to lead to a synthesis of trimethylbrazilin.—W.H.P., R.R.

retains considerable interest. Perkin and Robinson (T., 1908, **93**, 515) have already synthesised brazilinic acid and the lactone of dihydrobrazilinic acid, substances containing all the carbon atoms of brazilin, but in which the chromane and hydrindene rings are ruptured as the result of oxidation. Up to the present, no brazilin derivative has been synthesised that contains the characteristic fused ring system of the parent compound, nor does this skeleton occur in the molecule of any substance not itself obtained from brazilin or hæmatoxylin. We are now able to describe a simple method of synthesis of the *iso*brazilein salts, a result which harmonises with previous work and confirms the correctness of the view that brazilin is to be represented by the formula I.



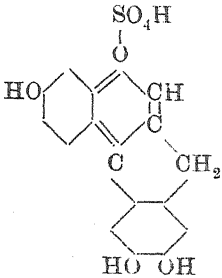
(I.)



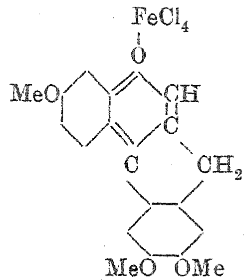
(II).

As is well known, brazilin, $C_{16}H_{14}O_5$, is converted by oxidation into the quinone brazilein, $C_{16}H_{12}O_5$ (II), and the latter was found by Hummel and A. G. Perkin (T., 1882, **41**, 367) to be transformed by mineral acids into a series of bright, orange-red salts which were called the *iso*brazilein salts. *iso*Brazilein hydrogen sulphate has the composition $C_{16}H_{11}O_4{\cdot}HSO_4$. Subsequently, these derivatives were examined by Engels, Perkin, and Robinson (T., 1908, **93**, 1121), who devised methods for the preparation of the methyl ethers of the salts and recognised the relation of the series to the anhydropyranol or pyrrylium oxonium salts. The constitutional formulæ III and IV were assigned to *iso*brazilein hydrogen sulphate and to the trimethyl ether of *iso*brazilein ferrichloride * respectively (*loc. cit.*).

* Engels, Perkin, and Robinson (*loc. cit.*) did not give names to these ethers which could be used to show their relation to brazilin. The difficulty is that *iso*brazilein, which is really *anhydro*brazilein and a quinone, contains only two hydroxyl groups and can yield only a dimethyl ether. The formation of a salt produces a further hydroxyl group from the quinonoid oxygen above, and it is possible to have a trimethyl ether of the salts. For this reason it is necessary to speak of *iso*brazilein ferrichloride trimethyl ether, and not of, what at first sight appears more natural, trimethyl*iso*brazilein ferrichloride. The systematic names are very cumbrous, the salt in question being 4 : 7 : 5′-trimethoxy-4 : 3-indeno-1 : 4-benzopyranol anhydroferrichloride.

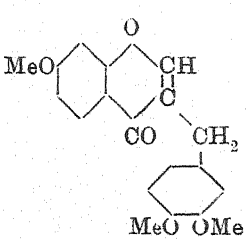


(III.)



(IV.)

Now, these particular derivatives of brazilin were obviously suitable objects of a synthetical investigation, partly on account of the vivid fluorescence which they exhibit under appropriate conditions, rendering the formation of a mere trace detectable, and also because the pyrrylium nucleus may be produced by the application of widely differing methods. We thought it very probable that the chromone derivative, V, would be converted into the trimethyl ether of an *iso*brazilein salt by the condensing action of acidic dehydrating agents, and our first attempts were accordingly directed towards the preparation of this substance by a method similar to that which had been employed for the synthesis of another 3-substituted chromone, namely, anhydrobrazilic acid (Perkin and Robinson, T., 1908, **93**, 504). Butein trimethyl ether (VI) (A. G. Perkin and Hummel, T., 1904, **85**, 1468) was obtained by the condensation of paeanol and veratraldehyde and reduced by the catalytic method to its dihydro-derivative (VII), but all attempts to convert this subsance into a pyrone by condensation with ethyl formate or ethyl oxalate by means of sodium or analogous agents were unsuccessful. It was observed, however, that the ketone, VII, exhibited a tendency to produce highly



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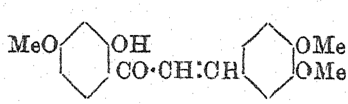
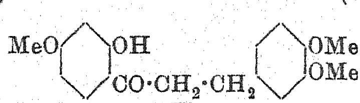


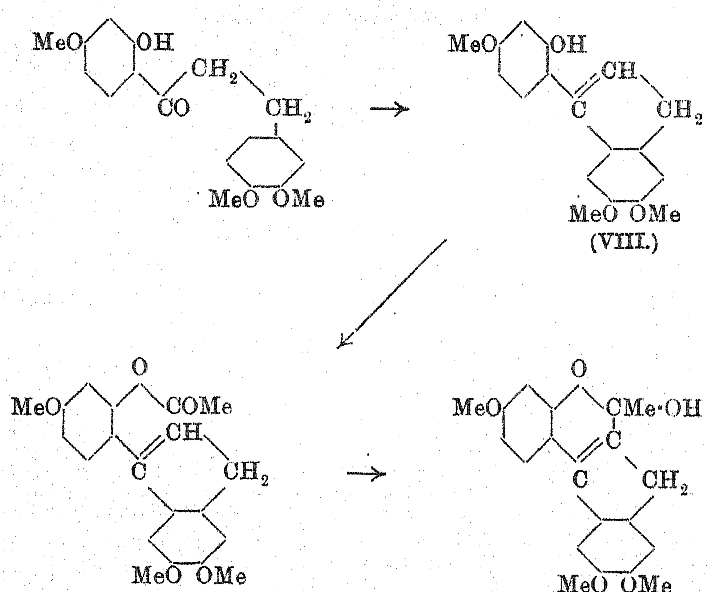
(VI.)



(VII.)

fluorescent substances when heated with acid anhydrides, and by boiling acetic anhydride in the presence of zinc chloride it was completely converted into an oxonium salt isolable in the form of its ferrichloride, and this product closely resembled the brazilin derivative, IV, especially in regard to the characteristic uranium-green fluorescence of its dilute aqueous solution.

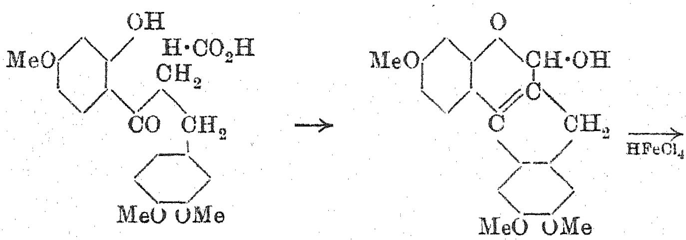
The conclusion that the substance is a homologue of *iso*brazilein ferrichloride trimethyl ether was supported by analytical data, and a whole series of similar salts may be obtained by replacing the acetic anhydride by other anhydrides. The synthesis probably occurs as represented below, but it is impossible to decide without further evidence whether indene-ring formation or acetylation is the first stage in the process. The final product indicated is an α-pyranol, which is converted by the action of acids into an *anhydro*-salt containing the pyrrylium nucleus. In this connexion we have included on p. 874 an account of some experiments made in 1909 by Mr. M. R. Turner, in collaboration with one of us, which go to show that an identical salt is obtained by the action of acid on corresponding α- and γ-*pyranols*.



(VIII.)

The action of dry hydrogen chloride, together with acetic anhydride and zinc chloride, on dihydrobutein trimethyl ether in the cold furnished a substance which is probably the indene derivative (VIII), and this is converted by the further action of hot

acetic anhydride and zinc chloride into the oxonium salt. The description of the foregoing compounds is reserved for a future communication. It was evident that in order to synthesise an *iso*brazilein salt, it would be necessary to introduce formic acid instead of acetic or other carboxylic acid in these reactions, and many attempts were made to utilise the mixed anhydride of formic and acetic acids in the hope that the phenol, VII, could be formylated and then further condensed in the desired direction. Unfortunately, this mixed anhydride, in the presence of salts such as zinc chloride or sodium acetate, or of acids or tertiary bases, decomposes too readily into carbon monoxide and acetic acid to be of great service as a reagent, and no progress was made along these lines. After numerous experiments in other directions, it was found that prolonged boiling of dihydrobutein trimethyl ether with a large excess of absolute formic acid and zinc chloride gave rise to a product from which *iso*brazilein ferrichloride trimethyl ether could be readily isolated. The synthesis is represented below:

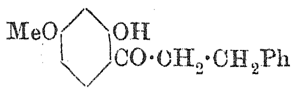


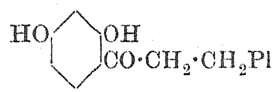
(IV.)

On heating the trimethyl ether salt* with hydrochloric acid at 150° in a sealed tube, a product was obtained which had all the reactions of *iso*brazilein hydrochloride. This demethylation will be further investigated if possible. The favourable issue of the research depended very largely on the devising of practical methods for the synthesis of hydrochalkone derivatives, and as a preliminary the processes available for the preparation of 2-hydroxy-4-methoxyphenyl phenylethyl ketone (IX) were compared. Bargellini and Marantonio (*Gazzetta*, 1908, **38**, ii, 514) obtained the corresponding dihydric phenol, 2:4-dihydroxyphenyl phenylethyl ketone (X), by the condensation of β-phenylpropionic acid with resorcinol by means of zinc chloride at 140—150°, and gave

* Before carrying out the demethylation, the ferric chloride was removed from the substance by conversion through the sparingly soluble orange-red sulphate into the hydrochloride. The sulphate was obtained by gently warming the ferrichloride with concentrated sulphuric acid and pouring into water. The process was repeated, and the hydrochloride obtained from the sulphate by the action of aqueous-alcoholic hydrochloric acid.

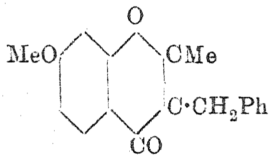
conditions under which it was claimed that it could be converted into either a monomethyl ether melting at 74—75° or a dimethyl ether melting at 103—104°.


(IX.)

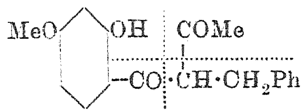

(X.)

As the result of our experiments, we are forced to the conclusion that the monomethyl ether melting at 74—75° does not exist, and that the so-called dimethyl ether is really the monomethyl ether. This substance crystallises from alcohol in needles melting at 105°; it contains only one methoxyl group, and may be obtained either by the methylation of the ketone, X, or by the reduction of benzylidenepaeanol. Its alcoholic solution gives a reddish-violet coloration with ferric chloride, but the phenolic function is weak, and the sodium salt is hydrolysed by water to such an extent that the substance may be completely extracted by ether from a suspension in aqueous sodium hydroxide. By far the best general method for the preparation of the hydrochalkone derivatives was found to be the reduction of the unsaturated ketones by hydrogen in the presence of a palladium sol or of palladium-black, and relatively small amounts of the catalyst were found to suffice. Benzylidenepaeanol could be reduced in alcoholic or ethereal solution, but veratrylidenepaeanol (butein trimethyl ether) was not reduced in those solvents or in ethyl acetate. It was, however, readily attacked in acetic acid solution. In the course of preliminary experiments we obtained one substance constituted similarly to the chromone, V. Kostanecki and Różycki (*Ber.*, 1901, **34**, 102) have shown that the acetylation of resacetophenone and of paeanol under correct conditions leads to the formation of chromone derivatives, and we have found that this reaction can be imitated in the case of benzylresacetophenone (X), but not with benzylpaeanol (IX). Acetic anhydride and sodium acetate at the boiling point of the mixture converts the former substance into the acetyl derivative of a hydroxybenzylmethylchromone, which is itself obtained on hydrolysis of the acetyl derivative, and may be converted in the usual manner into a methyl ether. The methyl ether is 7-methoxy-3-benzyl-2-methyl-1:4-benzopyrone (XI), as is proved by the fact that on hydrolysis by means of methyl-alcoholic potassium hydroxide it yields 2-hydroxy-4-methoxyphenyl phenylethyl ketone (IX), benzylacetone, and 2-hydroxy-4-methoxybenzoic acid. The formation of these substances is explicable as the result of the scission of the

primary product of hydrolysis (XII) in the two directions indicated by the dotted lines.



(XI.)

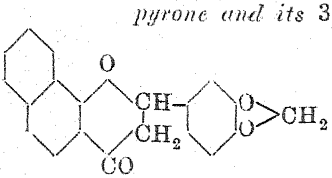


(XII.)

This chromone could not be converted into a salt of *iso*brazilein type, but many examples could be quoted to show that such an observation cannot safely be applied as a criterion of the probable behaviour of a corresponding veratryl derivative. The method which in this case was successfully used in the preparation of a 3-benzylchromone failed in the veratric series, because the condensation of resorcinol and 3:4-dimethoxyphenylpropionic acid in the presence of zinc chloride gave only tarry products.

EXPERIMENTAL.

3′:4′-*Methylenedioxy-2-phenyl-2*:3-*dihydro-1*:4-*α-naphthapyrone and its 3-Piperonylidene Derivative.*



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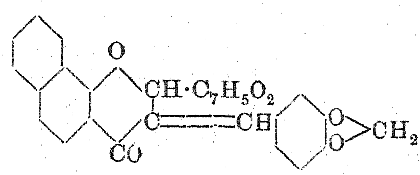


It has been pointed out on p. 861 that efforts were made to prepare 3-*homo*veratrylchromones, and among the possible methods seemed to be that depending on the realisation of the transference of a double bond in a veratrylidenechromanone from the *exo*cyclic to the *endo*cyclic position. As a preliminary case, the readily accessible substances figured above were prepared, but it was not found possible to convert the piperonylidene derivative into a true chromone by inducing a movement of the ethylene linking. Under varied treatment, the substance remained unchanged or suffered decomposition in other directions. The starting point in these experiments was 1-hydroxy-β-naphthyl methyl ketone

(2-acetyl-1-naphthol), and this was obtained by a slight modification of Friedländer's process (*Ber.*, 1895, **28**, 1946). An intimate mixture of α-naphthol (50 grams), acetic acid (75 grams), and zinc chloride (75 grams) was heated during thirty minutes at 160—170°. The precipitate obtained by the addition of water to the cooled mass was collected and washed with dilute hydrochloric acid, then dried, and crystallised from methyl alcohol. Three crystallisations gave a product melting at 99° (the pure substance melts at 103°), and this was sufficiently pure for most experiments. Our yield was always much diminished when we adopted the method of purification through the sodium salt, as recommended by Friedländer. Piperonylidenemethyl 1-hydroxy-β-naphthyl ketone (Kostanecki, *Ber.*, 1898, **31**, 707) was converted into the corresponding flavanone by a method similar to that frequently employed by Kostanecki and his co-workers. The unsaturated ketone (10 grams) was dissolved in hot alcohol (600 c.c.), and after the addition of concentrated hydrochloric acid (80 c.c.) and water (240 c.c.), the mixture was boiled under reflux during twenty-four hours. The solution was filtered hot, and, on cooling, the flavanone separated in pale orange needles, which were recrystallised from alcoholic hydrochloric acid, and then again twice from alcohol, when they were colourless and melted at 145°:

0·2460 gave 0·6792 CO_2 and 0·0974 H_2O. C=75·3; H=4·4.
$C_{20}H_{14}O_4$ requires C=75·5; H=4·4 per cent.

The substance is sparingly soluble in light petroleum, moderately so in methyl or ethyl alcohol, and dissolves freely in benzene, chloroform, acetone, or ethyl acetate.

Piperonylidene Derivative.—Owing to the ease with which the flavanone is reconverted by sodium hydroxide into the unsaturated ketone, it was necessary to employ an acid as the condensing agent in preparing this substance. The flavanone (2 grams) and piperonal (2 grams) were together dissolved in acetic acid (10 grams), and the solution was then saturated with hydrogen chloride. After allowing to remain overnight, the crystals which had separated were collected and crystallised from a mixture of nitrobenzene and alcohol. The substance was so obtained in rich golden balls of needles melting at 206°, and very sparingly soluble in most organic solvents:

0·1986 gave 0·5425 CO_2 and 0·0751 H_2O. C=74·5; H=4·2.
$C_{28}H_{18}O_6$ requires C=74·7; H=4·0 per cent.

The solution of this compound in sulphuric acid is intense reddish-purple. The nature of the dark green products obtained

by the action of vigorous acid condensing agents, such as phosphoryl chloride, could not be ascertained.

7-Hydroxy-3-benzyl-2-methyl-1 : 4-benzopyrone.

The acetyl derivative (see below) was boiled during two and a-half hours with an excess of dilute aqueous sodium carbonate, when it gradually dissolved as the result of hydrolysis. On cooling, the resulting phenol crystallised, and was collected and recrystallised from alcohol, being obtained in bundles of colourless, silky, prismatic needles melting at 282°:

0·1865 gave 0·5217 CO_2 and 0·0906 H_2O. C=76·3; H=5·4.
$C_{17}H_{14}O_3$ requires C=76·6; H=5·3 per cent.

The colourless solutions of the substance in cold aqueous sodium hydroxide or hot aqueous sodium carbonate exhibited violet fluorescence, and a similar appearance was obtained when the non-fluorescent solution in cold sulphuric acid was gently heated.

Acetyl Derivative.—2:4-Dihydroxyphenyl phenylethyl ketone (10 grams) was mixed with fused sodium acetate (15 grams) and acetic anhydride (20 grams), and heated in an oil-bath at 170° during four hours. Water and dilute hydrochloric acid were added to the cooled mass, and when the separated solid was free from acetic anhydride, it was collected, washed, dried, and crystallised from methyl alcohol, from which the compound separated in long, colourless needles melting at 121°:

0·2016 gave 0·5473 CO_2 and 0·0998 H_2O. C=74·0; H=5·5.
$C_{19}H_{16}O_4$ requires C=74·0; H=5·2 per cent.

The substance was not changed by dilute aqueous sodium hydroxide, and dissolved in sulphuric acid to a very pale yellow solution, which exhibited violet fluorescence on being heated.

Methyl Ether (XI).—7-Hydroxy-3-benzyl-2-methyl-1 : 4-benzopyrone (2 grams) was dissolved in hot methyl alcohol and mixed with methyl sulphate (5 c.c.). The solution was boiled under reflux, and aqueous potassium hydroxide (10 c.c. of 40 per cent.) gradually added during five minutes. The methyl ether was precipitated by the addition of water, but was not obtained in a satisfactory condition, and was therefore dissolved in ether, the ethereal solution washed with dilute sodium hydroxide, and dried. After the removal of the solvent, the oil solidified, and was crystallised from methyl alcohol, in which the substance is moderately readily soluble. The slender, colourless needles melted at 109°:

0·1675 gave 0·4722 CO_2 and 0·0859 H_2O. C=76·9; H=5·7.
$C_{18}H_{16}O_3$ requires C=77·1; H=5·7 per cent.

The solution in sulphuric acid is colourless and exhibits a faint blue fluorescence, which becomes intense on keeping or on gently heating, and this behaviour appears to be due to sulphonation. There was no evidence in numerous trials that the substance could be converted into a pyrrylium salt containing the indene nucleus.

Hydrolysis of the Methyl Ether.—A mixture of the methyl ether (1·5 grams), potassium hydroxide (2 grams), and methyl alcohol (10 c.c.) was heated in a wide test-tube in such a manner as gradually to remove a part of the methyl alcohol by distillation. A characteristic crimson coloration soon appeared and reached a maximum, after which it very quickly faded. When the solution or fusion had just lost the last trace of the red colour and had become yellow, the reaction was considered to be complete, and the mixture, together with the methyl-alcoholic distillate, was submitted to distillation in a current of steam. The aqueous distillate had the odour of benzylacetone, and the semicarbazone of the latter was prepared from it. This substance crystallised from alcohol in slender, colourless needles melting at 145° (Klages, *Ber.*, 1904, **37**, 2313, gives 142°), and at the same temperature when mixed with a purified specimen of the semicarbazone obtained from benzylacetone prepared by the reduction of phenyl styryl ketone by hydrogen in the presence of palladium. The alkaline solution remaining in the flask was rendered acid by the addition of hydrochloric acid, and then alkaline again with sodium carbonate. The oil precipitated by the acid did not redissolve, but soon solidified and was collected and crystallised from methyl alcohol, when it was obtained in colourless needles melting at 105°, and at the same temperature when mixed with a specimen of 2-hydroxy-4-methoxyphenyl phenylethyl ketone. The aqueous solution from which this substance had been separated was extracted with ether in order to remove further traces of the same compound; it was then concentrated and acidified, when a small amount of slender needles separated. The substance gave an intense violet colour with ferric chloride in aqueous solution, and melted at 155°. The melting point was not depressed when the substance was mixed with 2-hydroxy-4-methoxybenzoic acid obtained by the methylation of β-resorcyclic acid.

Methylation of Resacetophenone.

The following is a brief account of our observations in this connexion. The methylation to paeanol is advantageously effected by means of methyl iodide and potassium hydroxide in boiling methyl-alcoholic solution, and 10 per cent. more than the theoretically

required amount of each reagent suffices. If for each molecular proportion of resacetophenone three molecular proportions of methyl iodide and potassium hydroxide are employed, the main product is the dimethyl derivative, melting at 83—84° (Gregor, *Monatsh.*, 1894, **15**, 437; Wechsler, *ibid.*, **15**, 239; A. G. Perkin, T., 1895, **67**, 996), which has one of the methyl groups in the aromatic nucleus. An attempt was made to divide the operation of methylation into two parts, that is, to methylate first to paeanol and then to attempt the further conversion of this ether into the substance melting at 83—84°. When, however, paeanol was treated with two molecular proportions of methyl iodide and potassium hydroxide in boiling methyl alcohol, the greater part of the substance was recovered unchanged, and the small yield of product insoluble in cold sodium hydroxide solution was a mixture of about equal proportions of dimethylresacetophenone (m. p. 83—84°) and the normal dimethyl ether. The two substances could be separated by means of warm dilute sodium hydroxide, in which the former dissolves. This rather unexpected result renders it clear that the *C*-methylation of resacetophenone precedes the *O*-methylation in the case where an excess of methyl iodide and potassium hydroxide is employed. Probably the explanation is that, in the case of the dipotassium salt, methylation occurs at the carbon atom, whereas in the case of the monopotassium salt the *O*-ether is formed. If methyl sulphate is employed for the methylation, it is difficult to obtain a satisfactory yield of paeanol, and the substance melting at 83—84° is not obtained, but, instead, the normal dimethyl ether of resacetophenone.

A simple qualitative test which may be used to indicate the presence or absence of the nuclear methyl group in resorcinol derivatives of the type of resorcylic acid or resorcinol ketones depends on the formation of homofluorescein or fluorescein respectively. The substance is strongly heated with an excess of phthalic anhydride and a few drops of sulphuric acid, and the product dissolved in dilute sodium hydroxide. Fluorescein is formed under these conditions from most resorcinol derivatives, even if they are alkylated at the oxygen atom and the appearance of the alkaline solution is well known. If the resorcinol nucleus contains the methyl group, however, the alkaline solution is intense cherry-red, and the fluorescence is less persistent on dilution than is the case with fluorescein itself.

2-Hydroxy-4-methoxyphenyl Phenylethyl Ketone (IX).

We have carefully repeated the work of Bargellini and Marantonio (*loc. cit.*) on the methylation of 2:4-dihydroxyphenyl phenylethyl ketone, and have failed to obtain the so-called monomethyl ether melting at 74—75°. On the other hand, the prescription given for the preparation of the dimethyl ether works well, and the product is the real monomethyl ether. The substance crystallised from alcohol in colourless needles melting at 105°:

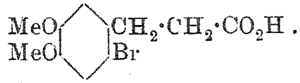
0·1635 gave 0·4491 CO_2 and 0·0927 H_2O. C=74·9; H=6·3.
0·4126 „ 0·3690 AgI. MeO=11·9.
$C_{16}H_{16}O_3$ requires C=75·0; H=6·3; MeO=12·1 per cent.

The same substance was obtained by the methylation of 2:4-dihydroxyphenyl phenylethyl ketone by means of half the theoretical amount of methyl sulphate, and also by employing methyl iodide. It was insoluble in aqueous sodium carbonate or sodium hydroxide in the cold, but dissolved in the latter on heating. It gives an intense reddish-violet coloration on the addition of ferric chloride to its alcoholic solution. Attempts to convert the substance into definite acetyl or benzoyl derivatives were unsuccessful, and we were unable to obtain its methyl ether. The constitution of the compound is best demonstrated by the following method of preparation.

Benzylidenepaeanol (Emilewicz and Kostanecki, *Ber.*, 1899, **32**, 312) could be reduced by hydrogen in the presence of palladium in ethereal or alcoholic solution, but the latter was more convenient in practice. The chalkone (5 grams) was dissolved in ethyl alcohol (250 c.c.) at from 50—60°, and the air in the flask containing the solution was then expelled by purified hydrogen, after which palladous chloride solution (15 c.c. of 1 per cent.) and gum arabic (15 c.c. of 1 per cent. solution) were added. The flask was then closed, vigorously shaken by mechanical means, and connected to the hydrogen generator.

The reduction proceeded rapidly and could easily be followed by noting the rapidity of the stream of hydrogen which passed through the wash-bottles. After twenty minutes, the gas was no longer absorbed, and this was coincident with the disappearance of the yellow colour of the alcoholic solution. The greater part of the alcohol was removed from the filtered solution by distillation, and, on cooling, the concentrate deposited 4·8 grams of needles melting at 105°. The substance melted at the same temperature when intimately mixed with a specimen obtained by the methylation of 2:4-dihydroxyphenyl phenylethyl ketone.

6-Bromo-3 : 4-dimethoxy-β-phenylpropionic Acid,



The condensation of 3 : 4-dimethoxyphenylpropionic acid and resorcinol in the presence of zinc chloride did not give useful results, probably owing to the ease with which the acid undergoes internal dehydration with the formation of dimethoxyhydrindone. It was thought that the bromo-acid would be more amenable in this reaction, but such did not prove to be the case.

3 : 4-Dimethoxyphenylpropionic acid was brominated in cold acetic acid solution by means of a molecular proportion of bromine dissolved in the same solvent. A part of the product crystallised and the remainder was obtained on the addition of water. The substance was crystallised from aqueous acetic acid and obtained in clusters of needles melting at 123°:

0·0916 required for neutralisation 0·01778 KOH.

This amount of a monobasic acid, $C_{11}H_{13}O_4Br$, requires 0·01772 KOH.

This acid is converted by phosphoric oxide in boiling benzene solution into a hydrindone derivative, which yields a very sparingly soluble piperonylidene derivative.

2-Hydroxy-4-methoxyphenyl 3 : 4-Dimethoxyphenylethyl Ketone (Dihydrobutein Trimethyl Ether), VII.

Veratrylidenepaeanol (A. G. Perkin and Hummel, *loc. cit.*) was found to be more difficult to reduce than the benzylidene derivative, and ether, alcohol, and ethyl acetate were all found to be unsuitable solvents. Ultimately, acetic acid was successfully employed, and the addition of a protective colloid, such as gum arabic, was omitted. The chalkone (5 grams), dissolved in acetic acid (450 c.c.), heated to 70—80°, was reduced by shaking with hydrogen after the addition of palladous chloride solution (20 c.c. of 1 per cent.). The absorption of gas slackened after half an hour, but, as the reaction did not appear to be complete, the liquid was again heated to 70—80° and 10 c.c. of the palladous chloride solution were added. The reduction was then completed by shaking with hydrogen for an hour. The colourless solution was filtered from the palladium-black and the acetic acid recovered by distillation under diminished pressure. Brine was added to the residue, and the colourless solid which was precipitated was collected, washed with water, and crystallised from methyl alcohol.

The substance crystallised in stout, colourless prisms melting at 84°, and the yield was 80 per cent. of that demanded by theory:

0·1400 gave 0·3512 CO_2 and 0·0879 H_2O. C=68·4; H=6·5.

$C_{18}H_{20}O_5$ requires C=68·4; H=6·3 per cent.

The coloration in alcoholic solution produced by the addition of a drop of ferric chloride is almost identical with that obtained in the case of ethyl acetoacetate. The substance is converted by dilute aqueous sodium hydroxide into a very sparingly soluble, voluminous sodium salt, but this is decomposed in the presence of ether, which extracts the free enol.

Synthesis of iso*Brazilein Ferrichloride Trimethyl Ether.*

A mixture of the compound just described (3 grams), fused zinc chloride (5 grams), and anhydrous formic acid (20 grams) was boiled for three hours under reflux. After a short time, the solution assumed a red colour and green fluorescence, and this became much intensified as the reaction proceeded. After cooling, dilute hydrochloric acid and an excess of concentrated ferric chloride solution were added, and a dark brown, viscid mass was precipitated. This was collected, freed as far as possible from adhering liquid, and then dissolved in hot acetic acid. As the solution cooled, pale brown, glistening needles with metallic glance separated, which were collected and purified by recrystallisation from acetic acid. Half a gram of the pure substance was obtained. In some respects, this synthesised material did not appear to be identical with *iso*brazilein ferrichloride trimethyl ether, which, as usually obtained (Engels, Perkin, and Robinson, *loc. cit.*, p. 1151), crystallises in magnificent copper leaflets, and it seemed at first sight necessary to conclude that the two substances were different. The reactions of the two specimens were, however, very similar, except with dilute aqueous sodium hydroxide, which in the case of the copper leaflets developed a reddish-purple colour. From previous experience, we surmised that this reaction must be due to the presence of phenolic groups, since the pyranol bases from methoxyanhydropyranol salts are colourless and insoluble in alkaline solutions. Since, in addition, microscopic examination of the copper leaflets showed that the crystals had curved edges, it became very probable that the substance obtained from brazilin was contaminated with a small proportion of a demethylated salt, the result of the action of the concentrated sulphuric acid used in the operation. This view was proved to be correct, since by exercising great care in the preparation we obtained the salt from brazilin in the same crystalline form as characterised the synthesised speci-

men. The tetramethyldihydrobrazileinol employed in the preparation was repeatedly purified by solution in light petroleum, as described by Engels, Perkin, and Robinson (*loc. cit.*), and ground in a mortar with excess of cold sulphuric acid for only ten minutes. The sulphate and hydrochloride were then isolated as already described, and the anhydroferrichloride was prepared from the latter in hot aqueous-alcoholic hydrochloric acid solution. The precipitated salt was recrystallised from acetic acid, and in this way a specimen was obtained which was identical in all respects with the material synthesised in the manner described above. The whole of the following observations were made with both specimens, and the two experiments carried out side by side and as nearly as possible under the same conditions. In all cases, complete identity of behaviour was recorded; all the colours appeared at the same stage; turbidity, fluorescence, and behaviour on dilution were always the same. The crystals are well-defined, pointed needles, transparent under the microscope, and in mass are pale ochreous-brown and have a coppery lustre. A suspension of the crystals in acetic acid has a characteristic appearance. If crystallised rapidly by cooling a concentrated solution in hot acetic acid, the tendency is for two or three needles to form a cluster, and at the ends of each of the larger needles a great number of very small needles collect. The substance has no definite melting point, it darkens at 180°, and above this temperature decomposition is progressive; from 203° to 215° there was shrinking and melting accompanied by decomposition. On breaking the capillary tubes, the contents were greenish-black and had a green lustre. The solubility of the substance in various solvents was noted. It does not dissolve in alcohol in the cold to any appreciable extent; on warming, the alcohol acquires an apple-green fluorescence, and, on boiling, the fluorescence is intense ivy-green and the solution becomes yellowish-brown. An aqueous solution of the substance is at first yellow and exhibits brilliant green fluorescence. On keeping, the salt is hydrolysed and the solution becomes slightly milky, the original appearance being restored by the addition of a few drops of hydrochloric acid. 0·1 Gram dissolves to a clear solution in 100 c.c. of water with the addition of 0·5 c.c. of concentrated hydrochloric acid. The behaviour of this solution on dilution was noted, and the fluorescence was found to be remarkably persistent. The addition of sodium acetate to the aqueous solution destroyed the fluorescence, and the pyranol base could be extracted by ether. The ethereal layer was very pale yellow, and the yellow, strongly fluorescent hydrochloride was regenerated by washing it with dilute hydrochloric acid. On the addition of nitric acid to the solution

of the substance in water, the first appearance was the loss of fluorescence and the production of a bright cherry-red colour. On keeping, the colour became yellow, and the fluorescence reappeared and was even more intense than that of the original solution. On the addition of sodium hydroxide to a solution of the ferrichloride, a faint cherry-red opalescence resulted; on shaking with air, a brownish-red solution and precipitate were obtained.

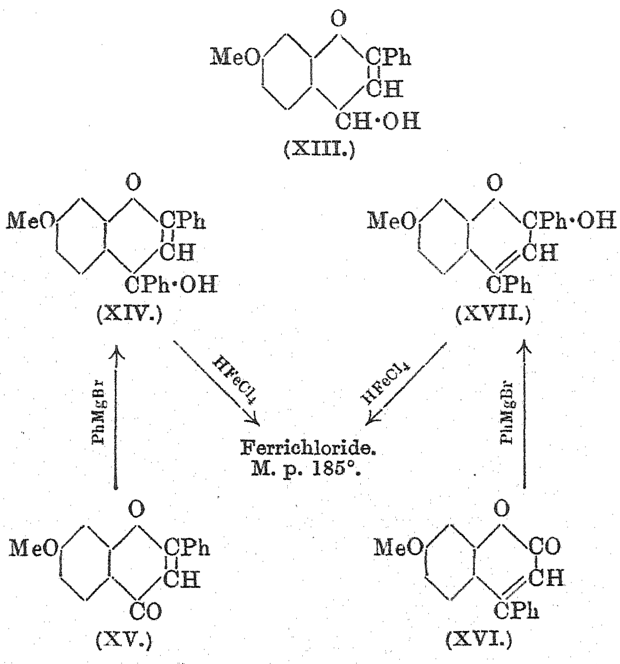
Appendix I.

Some Anhydropyranol Salts.

By Robert Robinson and Maurice Russell Turner.

About ten years ago the authors carried out a series of experiments in the benzopyranol group with the object of determining the nature of the pyranol bases and of discovering the cause of the intense colour which characterises some of these substances. It was found that the coloured pyranol bases are all quinones occasionally retaining tenaciously a molecule of water, and thus appearing to be carbinols. Several of these quinones were isolated in a pure condition, and it is hoped at some future time to publish an account of the investigation. In order to prove that the true carbinols are colourless, we prepared methyl ethers, and it is in connexion with these substances that certain points were noted which are of interest in relation to the foregoing communication. It is especially interesting that anhydro-salts of 7-methoxy-2-phenyl-1:4-benzopyranol (XIII) and of 7-methoxy-2:4-diphenyl-1:4-benzopyranol (XIV) dissolve in water with an intense bluish-green fluorescence, and in this respect closely resemble the similarly constituted *iso*brazilein hydrochloride trimethyl ether, but, on the other hand, differ from related hydroxy-compounds. The former substance (XIII) was obtained by the application of the general method for the preparation of anhydropyranol salts devised by Perkin, Robinson, and Turner (T., 1908, **93**, 1115), namely, by the condensation of 2-hydroxy-4-methoxybenzaldehyde with acetophenone in acetic acid solution by means of hydrogen chloride. The second compound (XIV) was obtained by the condensation of dibenzoylmethane with the monomethyl ether of resorcinol in the presence of sulphuric acid, but it was found impossible to obtain it by this method free from the corresponding demethylated compound, and the benzopyranol prepared from the salt was always red. This method of preparation has already been described by Becker and Decker (*Ber.*, 1914, **47**, 2288).

In order to obtain the substance in a pure condition, three methods could be employed, and are described on p. 877. As was to be expected, the compound (XIV) may be prepared by the action of magnesium phenyl bromide on 7-methoxy-2-phenyl-1:4-benzopyrone (XV), and was isolated from the product in the form of the anhydroferrichloride melting at 185°. The same anhydroferrichloride was, however, obtained from the product of interaction of magnesium phenyl bromide and β-phenylumbelliferone methyl ether (XVI). This would seem to demonstrate the possibility of the existence of two carbinol bases corresponding with a single anhydro-oxonium salt, since the process last mentioned should lead to the α-pyranol (XVII).



EXPERIMENTAL.

7-Methoxy-4-phenyl-1:2-benzopyrone (β-Phenylumbelliferone Methyl Ether), XVI.

A. A mixture of resorcinol monomethyl ether (13 grams) and ethyl benzoylacetate (20 grams) was dissolved in ice-cold sulphuric acid (200 grams). The flask was immersed in melting ice and allowed to remain for twelve hours. The viscid product obtained by dilution with water was well washed, and became solid in con-

tact with a little alcohol. The substance was collected and recrystallised from alcohol.

B. β-Phenylumbelliferone was methylated in the usual manner in methyl-alcoholic solution by means of methyl sulphate and potassium hydroxide. At the end of the reaction, however, an excess of hydrochloric acid was added and the solution boiled in order to convert into lactone any hydroxy-acid which had been formed as the result of the hydrolysing action of the alkali. After the addition of water, the substance was collected and crystallised from alcohol; it is moderately readily soluble in alcohol or benzene, and crystallises in slender needles which melt at 110°. The pale yellow solution in sulphuric acid exhibits intense bluish-violet fluorescence:

0·1255 gave 0·3489 CO_2 and 0·0560 H_2O. C=75·8; H=4·9.

$C_{16}H_{12}O_3$ requires C=76·2; H=4·7 per cent.

2:4-*Dimethoxydibenzoylmethane and* 7-*Methoxy*-2-*phenyl*-1:4-*benzopyrone* (XV).

2:4-Dimethoxydibenzoylmethane has already been obtained by Perkin and Schiess (T., 1904, **85**, 164) by the condensation of methyl 2:4-dimethoxybenzoate with acetophenone in the presence of metallic sodium. Since, however, we happened to be in the possession of large quantities of 2:4-dimethoxyacetophenone, we employed this compound as the starting point. 2:4-Dimethoxyacetophenone (55 grams) and ethyl benzoate (90 grams) were dissolved in dry ether (250 c.c.), and powdered sodamide (50 grams) was gradually added to the solution. A vigorous reaction ensued and the colourless sodium salt of the diketone separated as a crust. After gently boiling under reflux for half an hour, the salt was separated and washed with ether, and, when dry, was triturated in a mortar with dilute hydrochloric acid. The oily product soon became solid and crystalline in contact with fresh cold water, and was collected, washed with sodium carbonate solution, dried, and crystallised from light petroleum. The pale yellow needles melted at 57°:

0·1403 gave 0·3683 CO_2 and 0·0758 H_2O. C=71·6; H=6·0.

$C_{17}H_{16}O_4$ requires C=71·8; H=5·6 per cent.

When this diketone is mixed with ten times its weight of hot hydriodic acid (D 1·9), an immediate reaction occurs, methyl iodide is evolved, and the flavone derivative separates. The process is remarkably smooth. After removing the free iodine by the addition of sulphurous acid, the precipitate was collected and crystallised from alcohol. It melts at 110°, and is doubtless identical

with the compound obtained by Emilewicz and Kostanecki (*loc. cit.*) by the action of alkali on benzylidenepaeanol dibromide. The intensity of the blue fluorescence of the solution of this flavone in sulphuric acid is noteworthy.

7-Methoxy-2-phenyl-1:4-benzopyranol Anhydrohydrochloride. (Anhydrohydrochloride of XIII.)

2-Hydroxy-4-methoxybenzaldehyde (8 grams) and acetophenone (6 grams) were dissolved in glacial acetic acid (25 c.c.), and the solution was saturated with hydrogen chloride during an hour and a-half. The orange needles which separated were collected, and more of the substance was obtained by the addition of ether to the solution. The salt could be recrystallised from dilute hydrochloric acid, and, after being dried in the air, melted and decomposed at 102—103°:

0·1155 gave 0·2506 CO_2 and 0·0606 H_2O. C=59·2; H=5·8.

$C_{16}H_{13}O_2Cl,3H_2O$ requires C=58·8; H=5·8 per cent.

The substance dissolves in water to a yellow solution exhibiting a striking bluish-green fluorescence, extremely persistent on dilution.

7-Methoxy-2:4-diphenyl-1:4-benzopyranol and its Salts.

A. 7-Hydroxy-2 : 4-diphenyl-1 : 4-benzopyranol dimethyl ether (Bülow and Sicherer, *Ber.*, 1901, **34**, 2380) loses methyl alcohol on treatment with acids, and yields salts of the monomethylated pyranol. The ferrichloride was obtained in the usual manner, and crystallised from acetic acid in orange-yellow needles melting at 185°, and at the same temperature when mixed with the salt obtained as described under *B* and *C*. The fluorescence of the dimethyl ether in acetic or sulphuric acid solution is due to the conversion to an oxonium salt of the pyranol now under consideration.

B. β-Phenylumbelliferone methyl ether (2 grams) was dissolved in hot benzene (50 c.c.) and treated with a solution of magnesium phenyl bromide in ether until a test portion developed an intense bluish-green colour on the addition of an ethereal solution of *p*-benzoquinone. The mixture was then heated on the steam-bath for ten minutes, cooled, and decomposed with water. The benzene solution contained a substance which is probably an α-pyranol, and gave an oxonium salt on the addition of hydrochloric acid. In order to isolate this, the whole product was treated with dilute hydrochloric acid, and the separated yellow, aqueous layer mixed

with an excess of concentrated ferric chloride solution. The precipitated yellow ferrichloride was crystallised from acetic acid and obtained in orange needles melting at 185°.

C. 7-Methoxyflavone (4 grams) dissolved in benzene (150 c.c.) was mixed with an ethereal solution of magnesium phenyl bromide (from 1·8 grams of bromobenzene). A yellow precipitate was formed, and after gently heating on the steam-bath for fifteen minutes, the mixture was decomposed by dilute hydrochloric acid. A copious precipitate of the ferrichloride was obtained on the addition of ferric chloride to the aqueous layer, and the derivative was collected and crystallised from acetic acid. The orange-yellow needles melted at 185°:

0·1469 gave 0·2783 CO_2 and 0·0475 H_2O. C=51·7; H=3·6.
0·3600 „ 0·0572 Fe_2O_3. Fe=11·1.

$C_{22}H_{17}O_2Cl,FeCl_3$ requires C=51·7; H=3·3; Fe=11·0 per cent.

The pyranol itself and its derivatives could most conveniently be obtained by the method *A*.

7-*Methoxy*-2 : 4-*diphenyl*-1 : 4-*benzopyranol*.—Bülow and Sicherer's dimethyl ether was dissolved in dilute hydrochloric acid and the solution treated with sodium acetate. The almost colourless precipitate was amorphous, but was obtained in a pure condition by washing with water and drying in a vacuum over sulphuric acid. It melted at 55—57°:

0·1323 gave 0·3862 CO_2 and 0·0702 H_2O. C=79·6; H=5·9.
0·1962 in 19·9 benzene gave Δt=0·153°. M.W.=322.
$C_{22}H_{18}O_3$ requires C=80·0; H=5·5 per cent. M.W.=330.

Anhydrodihydrochloride.—Dry hydrogen chloride was passed through an ethereal solution of the pyranol. Bright yellow crystals melting at 121° separated, and were dried in a vacuum:

0·2264 gave 0·1576 AgCl. Cl=17·2.
$C_{22}H_{18}O_2Cl_2,2H_2O$ requires Cl=16·9 per cent.

Direct proof of the existence of the water of crystallisation was not obtained.

Anhydrohydrochloride.—The dihydrochloride was dissolved in hot dilute hydrochloric acid, and the solution, on cooling, deposited red needles melting indistinctly at about 80°:

0·2148 gave 0·0900 AgCl. Cl=10·4.
$C_{22}H_{17}O_2Cl$ requires Cl=10·2 per cent.

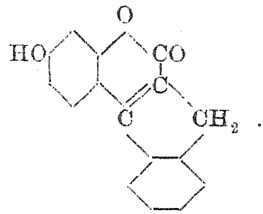
Anhydroplatinichloride.—This derivative was prepared in a hot solution, and crystallised, on cooling, in orange needles melting and decomposing at 224°:

0·2419 gave 0·0455 Pt. Pt = 18·8.

$(C_{22}H_{17}O_2Cl)_2PtCl_4$ requires Pt = 18·9 per cent.

Appendix II.

7-Hydroxy-4 : 3-indeno-1 : 2-benzopyrone,



This substance was prepared in 1911 by Mr. J. A. Prescott working in collaboration with one of us in the laboratories of the University of Manchester. Although the work was not carried far, it seems of interest to include a description of this substance in the present communication in view of the circumstance that it is the first compound to be synthesised the molecule of which contains the brazilin and hæmatoxylin skeleton.

α-Hydrindone (8·5 grams) dissolved in pure dry ether (100 c.c.) was converted into the sodium derivative by the addition of powdered sodamide (6 grams). The evolution of ammonia was facilitated by frequent shaking, and the reaction appeared to be complete in about two hours. A rather rapid stream of carbon dioxide was then passed through the solution until the ether had nearly all been removed by evaporation. Ice was then carefully added and the solution extracted twice with ether to remove a small amount of unchanged hydrindone. The separated aqueous layer was then acidified with hydrochloric acid with careful cooling by small pieces of ice. The crystalline precipitate was quickly collected and dried on porous porcelain. The yield of this *1-hydrindone-2-carboxylic acid* was 8 grams. The substance gives a reddish-violet coloration on the addition of ferric chloride to its aqueous or alcoholic solution. It is moderately stable at the ordinary temperature, but slowly decomposes with the formation of α-hydrindone and carbon dioxide. The reaction is rapid and complete on gently warming with water. The keto-acid (8·3 grams), together with resorcinol (9 grams), was mixed with a saturated solution (100 c.c.) of hydrogen chloride in methyl alcohol. The mixture was allowed to remain during two and a-half days at the ordinary temperature, when it became red, and a colourless substance crystallised. The liquid was then gently heated for two hours on the water-bath, and the quantity of the crystals was

increased. When cold, the substance was collected and crystallised from ethyl alcohol, from which it separated in colourless needles, the yield amounting to 2·1 grams:

Found: C=76·4; H=4·2.

$C_{16}H_{10}O_3$ requires C=76·8; H=4·0 per cent.

On heating, the substance darkens at about 230°, and at 280° rather suddenly turns dark blue, but does not melt at this or higher temperatures. It is sparingly soluble in most organic solvents, but dissolves in dilute sodium hydroxide. The solution in concentrated sulphuric acid exhibits an intense bluish-violet fluorescence.

UNIVERSITY OF LIVERPOOL. [*Received, September 23rd*, 1918.]

LXXIX.—*The Action of Chlorine on the Alkali Iodides.*

By WILLIAM NORMAN RAE.

IN a previous communication (T., 1915, **107**, 1286), an account was given of the action of bromine vapour on the solid iodides of the alkali metals, and the action of chlorine on the same compounds has now been studied.

The alkali metals form two series of polyhaloids containing both chlorine and iodine, having, respectively, the formulæ $MICl_2$ and $MICl_4$; all the compounds of the latter series were prepared in the wet way by Wells and Wheeler (*Amer. J. Sci.*, 1892, [iii], **44**, 42), who found that two of them gave hydrated crystals, namely, $LiICl_4,4H_2O$ and $NaICl_4,2H_2O$, whilst the others were anhydrous. The compounds $KICl_4$ and NH_4ICl_4 were originally prepared by Filhol (*J. Pharm.*, 1839, **25**, 435, 506).

In the present instance, the method of experiment was as follows: the iodides were powdered and kept in a desiccator over sulphuric acid for several weeks before using, to ensure thorough dryness; a small quantity was then placed in a weighing bottle having a ground-in glass stopper, through which passed two tubes, one of which reached nearly to the bottom of the bottle. During the weighings, the two tubes were closed with ground-in glass stoppers. Several of the bottles were connected in series, and a slow stream of chlorine, washed in water and dried with sulphuric acid, was passed through the train of bottles, and finally through

a calcium chloride tower, used to prevent moisture diffusing back in case the chlorine stream stopped. The bottles were weighed from day to day until the weight became constant, and the contents were then analysed. In all cases, the compound $MICl_4$ appeared to be formed. The compound $MICl_2$ for a given metal is much more stable than $MICl_4$, as is indicated by the well-marked breaks in the curves showing the loss of weight over potassium hydroxide with time, given in the previous paper (*loc. cit.*), and it might be expected that similar breaks would be obtained in the "increase of weight–time" curves in the present instance, the formation of the more stable compound $MICl_2$ proceeding more rapidly than that of the compound $MICl_4$. Such breaks, however, were not obtained, although there was a considerable diminution in the speed of the reaction towards the end, when the formation of the final compound was almost complete. Apparently the formation of the two compounds proceeds simultaneously, or the compound $MICl_4$ is formed without the intermediate formation of $MICl_2$; in this connexion, it may be remembered that Wells and Wheeler (*loc. cit.*) considered that the compound $RbICl_4$ decomposes at the ordinary temperature by the loss of iodine trichloride in one step, whilst at higher temperatures it loses first chlorine and then iodine monochloride; this is supported by the fact that when potassium tetrachloroiodide and mercury are placed in the same desiccator, mercuric iodide is formed. Again, it was expected that the stability of the various compounds would be indicated by the rate at which they were formed, but the reverse was the case; for example, in one experiment the first three tubes contained the iodides of cæsium, rubidium, and potassium, respectively; this is also the order of stability of the chloroiodides; after two days it was found that 1·27 grams of cæsium iodide had gained 0·10 gram, 0·65 gram of rubidium iodide had gained 0·40 gram, 1·67 grams of potassium iodide had gained 0·23 gram.

Several factors appear to affect the rate of formation besides the stability of the product; one of the most important is the degree of dryness of the solid iodide; an immediate increase in the rate of change follows the introduction of a trace of water, whilst lithium iodide, containing three molecules of water of crystallisation, always reacts rapidly. Rapid reactions are also obtained by using finely powdered solid in thin layers; with thick layers or crystals, the reaction takes place quickly at the surface, but only slowly throughout the mass.

The best quantitative results are obtained by using a slow stream of chlorine and a small quantity of solid; with larger quantities,

the initial displacement of the iodine in the iodide by chlorine proceeds rapidly, with the evolution of much heat (greatest in the case of lithium iodide and least with cæsium iodide), so that the liberated iodine is partly vaporised and is lost; at a slower rate, the temperature does not appreciably rise; with iodides such as those of rubidium and cæsium, the iodine at first set free appears to combine with the unchanged iodide to form the tri-iodides, which have a low vapour pressure. All the compounds obtained by this method are yellow powders; the colour shows a marked gradation with the atomic weight of the metal, the cæsium compound being a mustard-yellow, whilst that formed from lithium iodide is a fine deep orange.

Lithium Iodide.—The anhydrous compound has not been obtained in a pure state; the compound $LiI,3H_2O$ was therefore prepared, and the crystals, dried on filter-paper, were used, since the substance is too deliquescent to powder. At the same time, another part of the specimen was analysed. (Found: I=68·7. Calc., I=67·5 per cent.)

0·8526 Gram of the crystals gained 0·6549 gram of chlorine, a gain of 76·8 per cent., whilst the theoretical gain is 76·7 per cent. for the formation of $LiICl_4,xH_2O$ from LiI,xH_2O, containing 68·7 per cent. of iodine. On analysis by titration with arsenite solution, the amount of chlorine gained by the lithium iodide was found to be 71·8 per cent., and with a second preparation, 71·7 per cent.

When the chlorine first comes in contact with the lithium iodide, the latter becomes deep reddish-brown and moist on the surface; the crystals then melt and much heat is evolved, but there are no copious fumes of iodine chloride as there are in the case of iodine itself; liquid drops do appear on the sides, but these are only faintly coloured and are probably drops of moisture vaporised by the heat of the reaction. Finally, the whole is converted into an orange-coloured solid. The melting is due to the fact that the lithium iodide contains enough water to dissolve the lithium chloride which is formed at first, whilst both lithium iodide and the chloroiodide melt below 80°. The final compound is a solid at the ordinary temperature. Wells and Wheeler have shown that the crystals obtained from solution have the formula $LiICl_4,4H_2O$, whilst in the present case there is only enough water to give the compound $LiICl_4,3H_2O$. The reaction was complete in two days.

Ammonium Iodide.—The salt was recrystallised from water, and was then heated in an air-oven at 150° for some time, and was kept in the desiccator until required. Chlorine quickly changed it to bluish-black by displacing the iodine, and then the yellow

colour of the iodochloride appeared. The weight became constant in two or three days. 1·1512 Grams of ammonium iodide gained 1·1151 grams of chlorine, corresponding with 96·86 per cent., whilst the formation of NH_4ICl_4 requires a gain of 97·85 per cent. A determination of the extra halogen by the arsenite method gave a result corresponding with a gain of 95·94 per cent., a second preparation giving 94·99 per cent.

Sodium Iodide.—The salt was recrystallised from water in a desiccator over sulphuric acid. The crystals so obtained were powdered and replaced in the desiccator until used. The reaction followed a similar course to that with ammonium iodide, but a longer time was required to reach constant weight. In two experiments, 0·7587 gram gained 0·6927 gram, or 91·3 per cent., and 0·7956 gram gained 0·7439 gram, corresponding with 93·50 per cent; $NaICl_4$ requires a gain of 94·61 per cent. A specimen analysed by sodium arsenite gave 92·77 per cent.

Potassium Iodide.—The salt was recrystallised from water, dried, and powdered. Results similar to those with the previous two compounds were obtained, but in some cases a long time was required to reach constancy of weight. 1·0727 Grams of potassium iodide gained 0·9111 gram, equivalent to 84·94 per cent.; analysis by sodium arsenite gave extra halogen equivalent to a gain of 82·31 per cent., whilst the formation of $KICl_4$ requires 85·44 per cent.

Rubidium Iodide.—The salt was prepared by repeated evaporation of the chloride with hydriodic acid, and was then recrystallised from water. On coming in contact with chlorine, it first turned bluish-black and then yellow; in one experiment, the formation of the yellow compound did not commence simultaneously over the whole surface, but at a number of points, which appeared to act as nuclei, giving a very striking appearance of a number of bright yellow spots on a bluish-black background. 0·6545 Gram gained 0·4366 gram of chlorine, corresponding with 66·7 per cent., whilst $RbICl_4$ requires a gain of 66·8 per cent. Since very little of the rubidium salt was available, it was not analysed by sodium arsenite, but was heated until it was white. 1·0911 Grams of the chloroiodide lost 0·7234 gram of iodine trichloride, a loss of 66·3 per cent. In the conversion of the chloroiodide, $RbICl_4$, to rubidium chloride, the loss should be 65·9 per cent. The formation of the compound proceeded rapidly, and was complete in from three to six days.

Cæsium Iodide.—This salt was prepared in the same way as the rubidium compound; the first specimen made reacted very slowly; even the first stages, where the cæsium iodide was being converted

into the chloride, were slow, enabling the change of colour from white, through pale brown, brown, chocolate, to bluish-black to be followed. The pale brown colour observed at the start is possibly due to the formation of polyiodides, the first traces of iodine set free at once uniting with the unchanged cæsium iodide, so that the colour of free iodine is not observed until a later stage; the same colour is produced when solid cæsium iodide and iodine are shaken together. Compounds such as ammonium tri-iodide are much less stable than cæsium tri-iodide, which may account for the fact that the colour of iodine appears as soon as the chlorine comes into contact with ammonium iodide.

A more rapid reaction was obtained in an experiment using a small quantity of finely divided cæsium iodide, obtained by preparing the tri-iodide by crystallisation from solution and by heating this at 180° until it was quite white. 0·1986 Gram of cæsium iodide gained 0·1087 gram of chlorine in six days; the increase in weight corresponds with 54·7 per cent., which is the theoretical gain for the formation of $CsICl_4$. 0·3073 Gram of $CsICl_4$ lost 0·1794 gram on heating, corresponding with 58·3 per cent.; the theoretical loss is 58·1 per cent.

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[*Received, April 15th*, 1918.]

LXXX.—*Hydroxylamine Platinum Bases.*

By LEO ALEXANDROWITSCH TSCHUGAEV and ILJA ILJITSCH TSCHERNJAEV.

COMPOUNDS containing hydroxylamine and platinum were discovered by Lossen (*Annalen*, 1871, **160**, 242), and were studied in more detail by Alexander (*ibid.*, 1893, **246**, 239), and later by Ulenhuth (*ibid.*, 1900, **311**, 120).

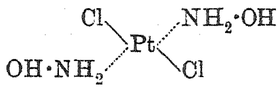
Hydroxylamine, like ammonia, combines with salts of bivalent platinum to form a series of complex compounds which are fairly closely analogous to the well-known ammoniacal platinum bases and to the corresponding derivatives of organic amines, sulphides, etc.

Free hydroxylamine and potassium platinochloride interact with the formation of tetrahydroxylaminoplatinous chloride,

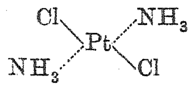
$$[Pt4NH_2{\cdot}OH]Cl_2,$$

an analogue of the salts of Reiset's Base I, $[Pt4NH_3]X_2$, and, like

these, this chloride is precipitated by potassium platinochloride to form the compound, $[Pt4NH_2{\cdot}OH]PtCl_4$, analogous to Magnus's green salt. Further, the chloride is decomposed by heating with hydrochloric acid, with the production of *trans*-dichlorodihydroxylaminoplatinum (*A*),



(*A*.)



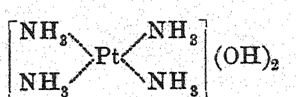
(*B*.)

which is similar, in its mode of formation and properties (see appendix), to the chloride of Reiset's Base II (*B*).

The study of these compounds has shown that hydroxylamine plays the same rôle in the molecule as does ammonia in ammoniacal platinum bases, this conclusion being confirmed by the existence of a mixed base, $[Pt2NH_3,2NH_2{\cdot}OH]X_2$, which may be regarded as Reiset's Base I with ammonia partly substituted by hydroxylamine. Some derivatives of this base are described, although very incompletely, by Alexander (*loc. cit.*).

In spite of the very close similarity between the hydroxylamine-platinum bases and the corresponding compounds containing ammonia in place of hydroxylamine, there is a marked difference in their chemical behaviour, as well as in their mode of formation. For example, hydroxylamine is more readily eliminated from the complex platinum compounds than ammonia; it was also not possible to obtain the *cis*-modification of dihydroxylaminoplatinous chloride, $[Pt2NH_2{\cdot}OH,Cl_2]$, in the usual way, namely, by the interaction of free hydroxylamine and potassium platinochloride, although the corresponding derivatives of ammonia and of organic amines are readily formed by a similar method.

Perhaps the most interesting fact to be noticed in this connexion is that by complete substitution of hydroxylamine for ammonia the very readily soluble compound $Pt4NH_3(OH)_2$, possessing strong basic properties and analogous to the alkali hydroxides, is transformed into the comparatively weak base $Pt4NH_2{\cdot}OH,(OH)_2$, almost insoluble in water and more similar to magnesia. For this reason, it was suggested by Werner ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., 5, 197) that a different constitution,



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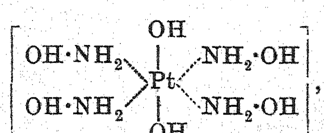


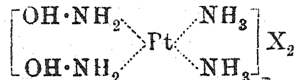
must be attributed to these two bases, the co-ordination numbers

being 4 in the case of Reiset's Base I and 6 in the corresponding hydroxylamine compound.

In view of the great interest attaching to these remarkable facts and relations, we decided to undertake a systematical investigation of the hydroxylamine-platinum bases, and particularly of the mixed bases containing hydroxylamine and ammonia (or amines), in order to elucidate the influence of the progressive substitution of hydroxylamine for ammonia.

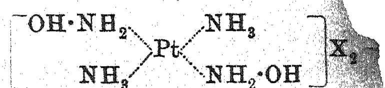
Of the six compounds theoretically possible and corresponding with the general formula $[Pt(NH_2{\cdot}OH)_n(NH_3)_{4-n}]X_2$, only three

$[Pt4NH_2{\cdot}OH]X_2$ (I.) $\left[Pt\begin{matrix}3NH_2{\cdot}OH\\NH_3\end{matrix}\right]X_2$ (II).



(III *A*.)

$[Pt4NH_3]X_2$ (V.) $\left[Pt\begin{matrix}NH_2{\cdot}OH\\3NH_3\end{matrix}\right]X_2$ (IV)



(III *B*)

(I, III*B*, and V) have been previously described.

We have succeeded in preparing all the missing members of the series, and have established their constitution and their relation t other hydroxylamino-ammoniacal platinum bases, so far as it v possible in the present state of our knowledge e chemical constitution of these complex compounds.

Considering first the two isomeric compounds corresponding with the formulæ III*A* and III*B*, the chloride of the former, namely, cis-*diamminodihydroxylaminoplatinous chloride* (III*A*, where X = Cl) may be prepared by the action of free hydroxylamine on *cis*-dichlorodiamminoplatinum (Peyrone's chloride).

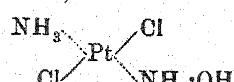
It contains the bivalent, colourless, complex cation

$$[Pt2NH_3,2NH_2{\cdot}OH]^{\cdot\cdot},$$

and gives a very characteristic platinochloride,

$$[Pt2NH_3,2NH_2{\cdot}OH]PtCl_4,$$

which forms rose-violet, microscopical needles. The constitution of the salts of this series is proved by their mode of formation, by the ionic character of the two electronegative radicles, and by the decomposition of the chloride with hydrochloric acid. In this reaction, the mixed chloride,

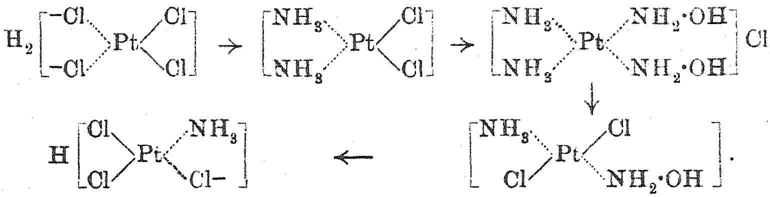


(VI.)

is formed in the first stage, and by continued action of the acid the second molecule of hydroxylamine is eliminated, Cossa's acid,

$[PtNH_3Cl_3]H$, and finally chloroplatinous acid, $H_2[PtCl_4]$, being obtained.

In view of the fact that Peyrone's chloride, the starting point in the preparation of the chloride III*A*, is prepared from chloroplatinous acid and ammonia, it will be seen that the synthesis of the salt III*A* and its degradation form a cycle, as represented by the following scheme:



In the same way, the isomeric salt III*B* may be obtained from the chloride of Reiset's Base II (*B*, p. 885), or by the action of liquid anhydrous ammonia on *trans*-dichlorodihydroxylaminoplatinum (*A*, p. 885).

Possibly the same chloride, in a slightly impure state, was prepared by Alexander by the interaction of *trans*-dichlorodihydroxylaminoplatinum and aqueous ammonia.

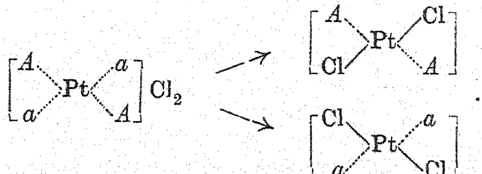
The existence of the bivalent complex cation,

$$[Pt2NH_3,2NH_2 \cdot OH]^{\cdot\cdot},$$

in an aqueous solution of the chloride III*B* may be proved by various reactions; for example, potassium platinochloride gives a green platinochloride, $[Pt2NH_3,2NH_2 \cdot OH]PtCl_4$, sparingly soluble in water, and potassium palladochloride and other salts of complex acids act similarly. The chlorine atoms of the chloride III*B* are both ionised in aqueous solution. From these facts, and especially from the mode of formation of this salt, its constitution as *trans-diamminodihydroxylaminoplatinous chloride* (III*B*, where X = Cl) may be regarded as sufficiently established.

The result of the action of hydrochloric acid on this substance is also in accordance with this conclusion, *trans*-dichlorodiamminoplatinum (*B*, p. 885) being the only product.

According to Jörgensen, the degradation of mixed complex bases corresponding with the *trans*-configuration gives normally two different products, both of which are *trans*-derivatives, thus:



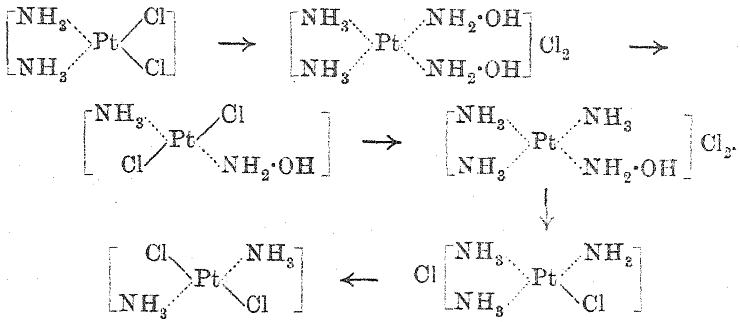
The degradation of the chloride III*B* proceeds, therefore, quite normally in so far as it gives rise to a *trans*-dichloro-derivative with two identical groups *A*, and the constitution assumed above for this chloride is especially confirmed by the fact that it gives the chloride of Reiset's Base II.

As regards the formation of only one product in this reaction instead of two, it may be remarked that the two compounds obtained by Jörgensen and by others in a series of analogous instances are generally produced in very different relative proportions, according to the degree of stability of the bond uniting the platinum atom with the molecule of ammonia or amine *A*. In fact, as will be seen later, it appears that a molecule of hydroxylamine is far more loosely combined with the platinum atom than is a molecule of ammonia, and apparently to this difference may be due the discrepancy between Jörgensen's rule and the course of degradation of the chloride III*B*.

Dichloroamminohydroxylaminoplatinum (VI, p. 886) is a very suitable starting point for the preparation of the two remaining members of our series of mixed ammonia-hydroxylaminoplatinum bases, namely, *amminotrihydroxylaminoplatinous chloride* (II, where X=Cl) and *triamminohydroxylaminoplatinous chloride* (IV, where X=Cl).

The chloride, IV, is best prepared by the interaction of dichloroamminohydroxylaminoplatinum (VI) and liquid ammonia in a sealed tube. Its constitution may be deduced from this mode of formation and from its chemical behaviour. The two chlorine atoms are immediately ionised in aqueous solution, and the complex radicle, $[Pt_3NH_3,NH_2{\cdot}OH]^{\cdot\cdot}$, has the properties of a bivalent cation. By treatment with potassium platinochloride, a green compound, $[Pt3NH_3,NH_2{\cdot}OH]PtCl_4$, analogous to the well-known Magnus's salt, is precipitated.

The most interesting results were obtained by the action of hydrochloric acid on the chloride (IV). The main product of this reaction is Cleve's chloride, $[Pt3NH_3Cl]Cl$, the molecule of hydroxylamine being displaced by a chlorine atom. This result not only proves the existence of the group $Pt3NH_3$ in the chloride, IV, but also affords a direct confirmation of the weakness of the bond $Pt...NH_2{\cdot}OH$ in comparison with the bond $Pt...NH_3$. A more energetic action of hydrochloric acid on Cleve's chloride results, as is well known, in the formation of the chloride of Reiset's Base II. Thus it is possible to effect the conversion of Peyrone's chloride into the isomeric chloride of Reiset's Base II by the following consecutive stages:



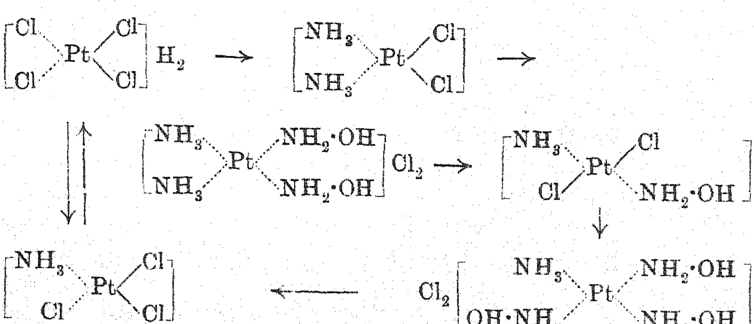
Amminotrihydroxylaminoplatinous chloride (II) is readily obtained from the chloride VI by the action of free hydroxylamine in aqueous solution. The constitution of this chloride follows from its mode of formation, from the inorganic character of the two chlorine atoms, and of the complex radicle, $PtNH_3,3NH_2{\cdot}OH$, which forms a bivalent cation (the platinochloride,

$$[PtNH_3,3NH_2{\cdot}OH]PtCl_4,$$

was obtained in rose-violet crystals), and especially from the study of its degradation products. By the action of hydrochloric acid, it gives Cossa's acid, $[PtNH_3{\cdot}Cl_3]H$, which then by further action of the acid furnishes chloroplatinous acid.

The relative weakness of the bond $Pt...NH_2{\cdot}OH$ is again demonstrated by this reaction.

It will be observed that the formation and degradation of the chloride, II, may also be represented by a cycle:



In addition to the above experiments, the behaviour of the *trans*-chloride, $[Pt2NH_2{\cdot}OH,Cl_2]$, towards pyridine was studied and found to be in perfect accordance with its behaviour towards ammonia.

The following table gives some physical properties of the mixed chlorides of the series $[Pt(NH_2{\cdot}OH)_n(NH_3)_{4-n}]Cl_2$:—

Compound.	Solubility. (Grams in 100 grams of 71·4 per cent. alcohol.)	Molecular conductivity at 25° V = 1000 litres.	Colour of the corresponding platinichloride.
$[Pt4NH_3]Cl_2$	—	261·0	Green (Magnus's salt)
$[Pt3NH_3,NH_2{\cdot}OH]Cl_2$	1·36	—	Green
$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2$ (*trans*)	0·136	251·0	Dark green
$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2$ (*cis*)	0·22	246·0	Reddish-violet
$[PtNH_3,3NH_2{\cdot}OH]Cl_2$	0·96	200·0	Rose-violet
$[Pt4NH_2{\cdot}OH]Cl_2$	0·28	—	Lilac

EXPERIMENTAL.

cis-*Diamminodihydroxylaminoplatinous Chloride* (III*A*, where X=Cl).

A mixture of 1 gram of Peyrone's chloride, 0·6 gram of hydroxylammonium chloride, 3·5 c.c. of 10 per cent. sodium hydroxide solution, and 7 c.c. of water was gently heated with frequent shaking until complete solution occurred. On cooling, the chloride separated in colourless needles or prisms, which were recrystallised from dilute hydrochloric acid and dried in the air:

0·1256 gave 0·0666 Pt. Pt=53·01.
0·2333 ,, 0·1855 AgCl. Cl=19·67.
0·1832 ,, 21·5 c.c. N_2 (moist) at 20·2° and 776 mm. N=15·32.
$PtH_{12}O_2N_4Cl_2$ requires Pt=53·27; Cl=19·37; N=15·30 per cent.

The substance is very readily soluble in water, the chlorine being completely ionised. The molecular conductivity was measured in aqueous solution at 25°:

V	125	250	500	1000
μ	226	232	239·5	276

The *platinochloride* separated from a solution of 0·65 gram of the above chloride in 5 c.c. of water on adding a solution of 0·8 gram of potassium platinochloride in 5 c.c. of water. It forms reddish-violet needles, and may be recrystallised from warm water. It is much more readily soluble than the green Magnus's salt.

The insoluble Magnus's salt is precipitated from its aqueous solution on the addition of Reiset's Base I,

$[Pt2NH_3,2NH_2\cdot OH]PtCl_4 + [Pt4NH_3]Cl_2 =$
$[Pt4NH_3]PtCl_4 + [Pt2NH_3,2NH_2\cdot OH]Cl_2$:

0·1119 gave 0·0675 Pt. Pt = 60·14.

$Pt_2H_{12}O_2N_4Cl_4$ requires Pt = 60·22 per cent.

The *palladochloride* was obtained from the chloride (III*A*) and potassium palladochloride. It separates as a dirty, green, microcrystalline powder sparingly soluble in water:

0·1053 gave 0·1107 AgCl. Cl = 26·06.

$PtPdH_{12}O_2N_4Cl_4$ requires Cl = 26·08 per cent.

trans-*Diaminodihydroxylaminoplatinous Chloride* (III*B*, where X = Cl).

This salt was prepared in the same manner as the *cis*-isomeride from the chloride of Reiset's Base II. It crystallises from hot water, in which it is readily soluble, in colourless prisms, and is precipitated from aqueous solutions by hydrochloric acid or alcohol:

0·1549 gave 0·0825 Pt. Pt = 53·24.
0·0944 ,, 0·0727 AgCl. Cl = 19·13.
0·1930 ,, 25·3 c.c. N_2 at 21° and 773 mm. N = 15·12.
$PtH_{12}O_2N_4Cl_2$ requires Pt = 53·27; Cl = 19·37; N = 15·30 per cent.

The chlorine atoms are both completely ionised, and are precipitated by silver nitrate. The following numbers were obtained for the molecular conductivity in aqueous solution at 25°:

V	250	500	1000
μ	229	240	251

The aqueous solution is neutral towards litmus, indicating the absence of appreciable hydrolysis. By heating the chloride with hydrochloric acid on the water-bath, as mentioned above, two molecular proportions of hydroxylamine are eliminated with the formation of the chloride of Reiset's Base II. (Found: Pt = 65·11. Calc.: Pt = 65·11 per cent.)

The *trans*-chloride may also be obtained by the interaction of *trans*-dichlorodihydroxylaminoplatinum, $[Pt2NH_2\cdot OH,Cl_2]$, and ammonia.

This reaction was first studied by Alexander (*loc. cit.*), who employed four molecular proportions of ammonia and one of the chloro-compound in aqueous solution, and obtained a flocculent, reddish-white precipitate, which he regarded as the free base, $[Pt2NH_2\cdot OH,2NH_3](OH)_2$. By dissolving it in cold dilute hydrochloric acid, he states that the chloride, $[Pt2NH_2\cdot OH,2NH_3]Cl_2$, was obtained, yielding a dark green platinochloride.

Alexander stated, further, that his chloride was precipitated by alkali hydroxides, yielding an amorphous, gelatinous mass insoluble in water. On the other hand, his chloride was very unstable towards concentrated hydrochloric acid, which decomposed it with the loss of two molecular proportions of ammonia and the formation of *trans*-dichlorodihydroxylaminoplatinum.

The properties of this substance being thus entirely different from the properties of the chloride described above, we decided to repeat the corresponding part of Alexander's work. It appeared from our experiments that, under the conditions mentioned by this author, ammonia indeed gives with the compound

$$[Pt2NH_2{\cdot}OH,Cl_2]$$

an insoluble, amorphous, pale yellow precipitate, but this is by no means formed by the addition of ammonia to dichlorodihydroxylaminoplatinum. On the contrary, its composition corresponds approximately with the formula $[PtNH_2{\cdot}OH,Cl(OH)]$ of a hydroxo-compound, one atom of chlorine being displaced by a hydroxyl group, and, as was to be expected, we were unable to obtain from this substance the mixed chloride,

$$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2,$$

by the action of hydrochloric acid.

The addition of ammonia to the compound $[Pt2NH_2{\cdot}OH,Cl_2]$, may be easily effected by using anhydrous liquid ammonia and by operating in a sealed tube. An orange solution is obtained at first, which is gradually decolorised. At the same time, a colourless, crystalline precipitate of the chloride,

$$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2,$$

separates. The composition of the substance was verified by analysis, and its identity with the *trans*-isomeride was proved by its characteristic reactions. It was specially ascertained that this chloride yielded, on heating with with hydrochloric acid, the chloride of Reiset's Base II. *trans*-Dichlorodihydroxylaminoplatinum could not be obtained under these conditions.

The *platinochloride* of the salt just described may be obtained by the addition of potassium platinochloride to its solution; it forms microscopic, dark green needles, which are sparingly soluble in cold water and may be recrystallised from hot water containing a little hydrochloric acid. It is much more stable than the *cis*-isomeride:

0·0714 gave 0·0438 Pt. Pt=61·40.
0·1335 „ 10·5 c.c. N_2 (moist) at 21° and 773 mm. N=9·07.
$Pt_2H_{12}O_2N_4Cl_4$ requires Pt=61·75; N=8·86 per cent.

The *palladochloride*, similarly prepared by the aid of ammonium palladochloride, forms microscopic, olive-green needles:

0·0665 gave 0·0698 AgCl. Cl=26·00.

$PtPdH_{12}O_2N_4Cl_4$ requires Cl=26·08 per cent.

trans-*Dichloroamminohydroxylaminoplatinum* (VI, p. 886).

One gram of the *cis*-chloride, $[Pt2NH_3,2NH_2\cdot OH]Cl_2$, is heated on the water-bath for one and a-half hours with 5 c.c. of hydrochloric acid (D 1·19) and 20 c.c. of water. The colour of the solution must remain yellow; if it turns orange-red, the reaction has proceeded too far. On cooling, the mixed compound separates in characteristic aggregates of dentate yellow crystals, which may be recrystallised from very dilute hydrochloric acid. The yield is 70—90 per cent. of the theoretical:

0·0934 gave 0·0576 Pt. Pt=61·64.
0·1578 „ 12·4 c.c. N_2 (moist) at 20° and 756 mm. N=8·91.
0·1119 „ 0·1004 AgCl. Cl=22·19.
$PtH_6ON_2Cl_2$ requires Pt=61·75; N=8·76; Cl=22·43 per cent.

The substance is sparingly soluble in cold, but much more readily so in hot water, and very sparingly so in alcohol.

The aqueous solution is greenish-yellow, and immediately after the addition of silver nitrate gives only a slight opalescence, the precipitation of silver chloride occurring only gradually and being accelerated by heating.

It must accordingly be assumed that the chlorine atoms are in direct union with the platinum. This conclusion was confirmed by the determination of the molecular conductivity (in aqueous solution at 25°), which gave very low values almost approaching zero: $\mu=2\cdot05$ (V=526). The values of μ rise very quickly with time, hydrolysis evidently taking place under these conditions.

By the prolonged action of hot hydrochloric acid, the substance is decomposed with the elimination of one molecular proportion of hydroxylamine and formation of the complex acid, $[PtNH_3,Cl_3]H$, discovered by Cossa:

$$[PtNH_3,NH_2\cdot OH,Cl_2]+2HCl=(PtNH_3,Cl_3)H+NH_2\cdot OH,HCl.$$

This acid was identified by precipitating the solution with the chloride of Reiset's Base I. The characteristic orange-yellow quadratic scales of Cossa's salt, $[PtNH_3,Cl_3]_2[Pt4NH_3]$, were obtained, and its composition was verified by analysis. (Found: Pt=64·92. Calc.: Pt=65·10 per cent.)

Triamminohydroxylaminoplatinous Chloride,
$[Pt(NH_3)_3,NH_2{\cdot}OH]Cl_2$.

This substance was prepared by the interaction of the mixed salt just described and anhydrous liquid ammonia in a sealed tube at the ordinary temperature. After the expulsion of free ammonia, a colourless, crystalline powder remained which crystallised from 80 per cent. alcohol in colourless, glistening plates very readily soluble in water:

0·1206 gave 0·0673 Pt. Pt=55·83.
0·0950 ,, 0·0781 AgCl. Cl=20·34.
0·1436 ,, 20·1 c.c. N_2 (moist) at 21° and 770 mm. N=16·07.
$PtH_{12}ON_4Cl_2$ requires Pt=55·73; Cl=20·25; N=16·00 per cent.

On heating with hydrochloric acid, the substance is decomposed, hydroxylamine being eliminated and Cleve's salt, $[Pt3NH_3,Cl]Cl_2$, being formed, which was detected by means of its very characteristic platinochloride, $[Pt3NH_3,Cl]_2PtCl_4$.

The *platinochloride*, $[Pt3NH_3,NH_2{\cdot}OH]PtCl_4$, was obtained by precipitating the preceding chloride with potassium platinochloride, as a pale green powder consisting of microscopic needles which may be recrystallised from hot water:

0·1001 gave 0·0634 Pt. Pt=63·34.
0·2186 ,, 17·4 c.c. N_2 (moist) at 21° and 773 mm. N=9·17.
0·1103 ,, 0·1038 AgCl. Cl=23·28.
$Pt_2H_{12}ON_4Cl_4$ requires Pt=63·34; N=9·10; Cl=23·01 per cent.

By heating this platinochloride with hydrochloric acid, hydroxylamine is eliminated, and the characteristic pink plates of Cleve's salt, $[Pt3NH_3Cl]_2PtCl_4$, separate, especally on cooling, together with unchanged substance. The separation of the two can be effected by levigation and by subsequent recrystallisation from very dilute hydrochloric acid.

Amminotrihydroxylaminoplatinous Chloride,
$[PtNH_3,(NH_2{\cdot}OH)_3]Cl_2$.

The mixed chloride, $[PtNH_3,NH_2{\cdot}OH,Cl_2]$, was gently heated with the theoretical quantity of hydroxylamine hydrochloride and the equivalent quantity of sodium hydroxide in aqueous solution. The new chloride is very readily soluble in water, and may be separated from a concentrated aqueous solution by the addition of alcohol or of hydrochloric acid. It forms transparent, colourless crystals:

0·1061 gave 0·0542 Pt. Pt = 51·03.
0·1126 ,, 14·4 c.c. N_2 (moist) at 19·4° and 765·5 mm. N = 14·68.
0·1058 gave 0·0788 AgCl. Cl = 18·42.
$PtH_{12}O_3N_4Cl_2$ requires Pt = 51·07; N = 14·67; Cl = 18·55 per cent.

The chlorine atoms are both completely ionised. The figures obtained for the molecular conductivity at 25° are: V = 1000; μ = 240.

The *platinochloride*, precipitated from a solution of the preceding salt by means of potassium platinochloride, forms microscopic, rose-violet needles:

0·1119 gave 0·0675 Pt. Pt = 60·14.
$Pt_2H_{12}O_3N_4Cl_4$ requires Pt = 60·22 per cent.

The *palladochloride*, similarly obtained from ammonium palladochloride, crystallises in reddish-violet needles:

0·0567 gave 0·0587 AgCl. Cl = 25·62.
$PtPdH_{12}O_3N_4Cl_4$ requires Cl = 25·37 per cent.

trans-*Dipyridinodihydroxylaminoplatinous Chloride*,

$$\left[\begin{array}{ccc} & Py & NH_2\cdot OH \\ & & Pt \\ OH\cdot NH_2 & & Py \end{array}\right] Cl_2.$$

This substance was prepared by the interaction of pyridine and *trans*-dichlorodihydroxylaminoplatinum. Dry pyridine readily dissolves the dichloro-compound, forming an orange-yellow solution, which loses its colour very quickly, and at the same time a colourless, crystalline powder separates. The mixture is heated for some minutes and filtered after cooling. The residue is then washed with alcohol and recrystallised from hot water:

0·0986 gave 0·0392 Pt. Pt = 39·76.
0·1133 ,, 0·0649 AgCl. Cl = 14·1.
$C_{10}H_{16}O_2N_4Cl_2Pt$ requires Pt = 39·80; Cl = 14·4 per cent.

Potassium platinochloride precipitates the platinochloride, $[Pt2Py,(NH_2\cdot OH)_2]PtCl_4$, which crystallises in microscopic, pale rose prisms:

0·1450 gave 0·0746 Pt. Pt = 51·41.
$C_{10}H_{16}O_2N_4Cl_4Pt_2$ requires Pt = 51·61 per cent.

On heating with hydrochloric acid, *trans*-dipyridinodihydroxylaminoplatinous chloride behaves in a similar manner to the corresponding ammonia compound; the substance loses two molecular proportions of hydroxylamine and dichlorodipyridinoplatinum is

formed. (Found: Pt=45·78. Calc.: Pt=46·03 per cent.) This substance possesses all the properties assigned to it by Jörgensen (*J. pr. Chem.*, 1886, [ii], **33**, 489).

Appendix.

trans-*Dichlorodihydroxylaminoplatinum* (*A*, p. 885).

This substance, as stated by Alexander, is easily obtainable from the tetrahydroxylamine compound, $[Pt4NH_2{\cdot}OH]Cl_2$, by heating it with dilute hydrochloric acid, and separates from the solution, on cooling, in large orange needles or prisms.

In complete accordance with Werner's theory, it possesses the property of a typical non-electrolyte, for it gives only a slight opalescence immediately after the addition of silver nitrate to its aqueous solution, whilst the complete precipitation of silver chloride is effected only after a long time, but very quickly by heating. The conductivity measurements gave also, as was to be expected, very low figures approaching zero: $V=287$ ($t=25°$); $\mu=1{\cdot}25$.

A more thorough study of this substance showed that it has the property of forming double compounds with certain chlorides, such as the chloride of Reiset's Base I and cæsium chloride.

Two grams of the compound, $[Pt2NH_2{\cdot}OH,Cl_2]$, and 2 grams of the chloride, $[Pt4NH_3]Cl_2$, were dissolved in 6 c.c. of hot water. On cooling, the additive compound separated in well-defined, pale yellow, prismatic crystals fairly readily soluble in water, the composition of which corresponds with the formula

$$[Pt2NH_2{\cdot}OH,Cl_2].[Pt4NH_3]Cl_2,2H_2O:$$

1·4070 gave 0·0722 H_2O. $H_2O=5{\cdot}13$.
0·2357 „ 0·1309 Pt. Pt=55·54.
$Pt_2H_{18}O_2N_6Cl_4,2H_2O$ requires $H_2O=5{\cdot}13$; Pt=55·58 per cent.

The water is eliminated at 100—110°, but not in a vacuum desiccator over sulphuric acid (the anhydrous salt gave Pt=58·51; Calc.: Pt=58·58 per cent.).

The double compound with cæsium chloride,

$$[Pt2NH_2{\cdot}OH,Cl_2],2CsCl,$$

was obtained in a similar manner and has almost the same properties:

0·1658 gave 0·1684 Cs_2PtCl_6. Cs=40·08.
0·1854 „ 0·0544 Pt. Pt=29·34.
0·1659 „ 0·1435 AgCl. Cl=21·40.
$PtCs_2H_6O_2N_2Cl_4$ requires Cs=39·76; Pt=29·15; Cl=21·22 per cent.

The existence of these double compounds may be considered as an indication of the property possessed by the non-electrolyte,

$[Pt2NH_2{\cdot}OH,Cl_2]$, of combining with two chlorine ions to yield the unstable complex anion, $[Pt2NH_2{\cdot}OH,Cl_4]''$.

Accordingly, the constitution of the double compounds may be represented by the formulæ $[Pt2NH_2{\cdot}OH,Cl_4][Pt4NH_3]$ and $[Pt2NH_2{\cdot}OH,Cl_4]Cs_2$.

THE UNIVERSITY,
PETROGRAD.

[*Received June 24th*, 1918.]

LXXXI.—*Trimorphic Change of 4-Nitroaceto-o-toluidide.*

By FREDERICK DANIEL CHATTAWAY.

CASES of trimorphic change, although several have been observed, are sufficiently rare for a new one to be of interest. The phenomenon is well shown by 4-nitroaceto-*o*-toluidide, which on crystallisation undergoes two successive transformations before a stable state is reached.

By nitrating *o*-toluidine in the presence of excess of concentrated sulphuric acid, Nölting and Collin (*Ber.*, 1884, **17**, 269) first prepared the base, and by heating with acetic anhydride converted it into the acetyl derivative. This they describe very briefly as crystallising in yellowish-white needles melting at 150—151°.

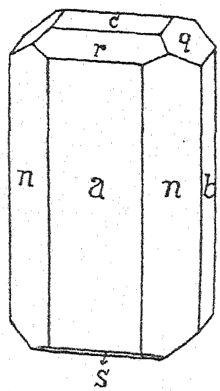
Speaking in general terms, all anilides crystallise in one of three easily recognisable forms, namely, a slender prismatic form, a compact form, and a hair-like form, and many have been obtained in two of them.

4-Nitroaceto-*o*-toluidide can be obtained in all three forms, the order of stability being: slender prismatic $\longrightarrow$ compact $\longrightarrow$ hair-like.

It is moderately readily soluble in boiling alcohol, giving a pale yellow solution, from which very slender prisms of the first, or α-form, separate on cooling. These are of such a pale yellow colour that when dry they appear almost colourless. If the original solution is sufficiently concentrated, they grow until the whole liquid is filled with a mass of slender crystals, generally radiating from a few points. If these crystals are allowed to remain in the mother liquor at the ordinary temperature, small, yellow, six-sided plates of the second, or β-modification, soon make their appearance, and rapidly grow at the expense of the first form, which dissolves in their neighbourhood, forming cavities occupied by one or more crystals that may increase to a considerable size

and are usually well shaped. The transformation into the second form is generally complete after the lapse of a few days if the beaker is left undisturbed, although the time taken depends greatly on the average temperature, and is much shortened by occasionally shaking the transforming mass. When the change is complete, a relatively thin layer of well-shaped, compact crystals remains at the bottom of the beaker.

After some time, often before complete transformation of the first into the second form, a third, or γ-modification, makes its appearance in tufts of colourless, hair-like crystals resembling small colonies of a mould or tiny balls of cotton wool. These increase in size, the compact form dissolving and disappearing until the whole contents of the beaker become a felted mass having a superficial resemblance to a somewhat slimy jelly. From this, the mother



liquor is removed only with difficulty by filtration or pressure. Direct transformation of the α- into the γ-form occurs if the mass of slender prismatic crystals first separating is seeded with a few crystals of the hair-like form.

All three forms, when heated, soften and melt at the same temperature, namely, 150—151°, which seems to indicate that before the fusion point is reached transformation into the form most stable near that temperature takes place.

Mr. T. V. Barker, who has very kindly examined the crystals, reports on them as follows.

The first, or α-modification, crystallises in doubly refracting needles with straight extinction.

The well-developed crystals of the β-modification belong to the monoclinic system. Forms: $a(100)$, $c(001)$, $n(210)$, $b(010)$, $q(011)$, and $r(101)$; also, occasionally, $s(\bar{1}01)$, and, very rarely, $x(021)$ and

$y(012)$. The general habit and common forms of the crystals are shown in the figure. Crystallographic constants: 57°26′, a(48°34′)m(41°26′)b, 49°43′, 74°10′, or, alternatively, $a:b:c=$ 1·178 : 1 : 0·6388, β=105°50′. Three crystals were measured on the two-circle goniometer; following are the mean values of the most trustworthy results:

	b (010).	a (100).	n (210).	c (001)
Azimuth	Face of	0° 0′	0° 0′	*74° 10′
Polar distance ...	reference	90 0	*60 28	90 0

	q (011).	r (101).	
Azimuth	74° 10′	50° 13′	(calc. = 49° 43′)
Polar distance ...	*58 25½	90 0	

Optically, biaxial; axial plane, b(010); extinction on b(010), 37° with prism edge in the obtuse angle β. Complex-symbol: $4h\,;+16/42/+3\frac{1}{2}$.

The third, or γ-modification, crystallises in hair-like, doubly refracting needles with an extinction of 35°.

UNIVERSITY CHEMICAL LABORATORY,
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LXXXII.—*The Preparation of Ethylamine and of Diethylamine.*

By EMIL ALPHONSE WERNER.

IN the preparation of ethylamine and of diethylamine by the interaction of ethyl bromide and ammonia, it has been the usual practice, so far as hitherto recorded, to submit the whole of the alkyl haloid to the action of ammonia in a single operation.

This is a faulty procedure, since it conduces largely to the formation of the less useful triethylamine, with consequent loss in the yields of the primary and secondary bases. Whether the change is promoted by heat or is allowed to proceed at the ordinary temperature, the tertiary amine has been present in largest amount in the final product (compare Garner and Tyrer, T., 1916, **109**, 174).

The author has found that when ethylamine is added to an alcoholic solution of diethylammonium chloride, the displacement of the secondary amine by the primary is quantitative; thus

diethylamine only was obtained on distillation of the mixture after it had remained for an hour, whilst under similar conditions the displacement of triethylamine from its hydrochloride by diethylamine was likewise quantitative (Expts. I, II).

A fair separation of all three amines, in the same order, has been effected by fractional treatment of a solution of their salts with sodium hydroxide; the tertiary amine was first liberated, the secondary next, and the primary amine last (Expt. III).

It must be admitted that these results go to show, contrary to the commonly accepted view, that triethylamine is the weakest base of the three amines.

Reasoning on this basis, and bearing in mind the relative tendency to dissociation* of the respective 'amine' salts, a procedure has been adopted whereby the formation of triethylamine has been almost completely suppressed. Thus, from the product of two experiments, in which 2090 grams of ethyl bromide were used, only 27 grams of triethylamine were obtained, whilst the yield of ethylamine was 33·8 per cent. and of diethylamine 57·5 per cent. of the theoretical.

The influence of the proportion of ammonia to ethyl bromide on the yield of ethylamine is shown by the following results:

Molecular ratio $EtBr : NH_3$	1 : 1	1 : 4	1 : 6	1 : 8	1 : 16
Percentage yield of NH_2Et on theoretical	11·3	24·4	26·7	28·1	34·2

The necessity of maintaining a good excess of ammonia throughout the progress of the reaction is indicated by theory.

Experimental.

Preparation of Ethylamine and of Diethylamine.

Five litres of 90 per cent. alcohol were saturated with ammonia (compare this vol., p. 698) until 490 grams of the gas had been dissolved, 200 grams of ethyl bromide were added (ratio EtBr to NH_3 approximately 1 to 16), after which, at successive intervals of two days, fresh quantities of the alkyl haloid were added in the following amounts: 180, 170, 150, 130, 110, 100, 80, and, finally, 66 grams. Preliminary experiments had shown that with the above ratio of ammonia the whole of the ethyl bromide was decomposed after two days, hence the successive quantities were regulated

* The term as used here does not refer to ionisation or electrolytic dissociation.

so as to maintain the desired excess of ammonia throughout the progress of the change. In all, 1186 grams of ethyl bromide were used; ammonium bromide began to separate on the twelfth day, and on the sixteenth day the preparation was stopped. Test experiments on a small scale with pure alcohol had shown that when ammonium bromide separated in quantity in the early stage of the process, the formation of triethylamine was promoted when the reaction was prolonged. The reason is fairly obvious when the probable mechanism of the process is considered, hence it was found advantageous to use alcohol containing 10 per cent. of water.

The alcoholic solution, separated from ammonium bromide, was concentrated by distillation (the ammonia evolved was used to charge more alcohol) until nearly all the ammonium bromide formed had separated, 362 grams of which were recovered.

The solution of the hydrobromides of the mixed amines was distilled until the temperature reached 130°, in order to remove the last traces of alcohol. Where it was not found convenient to liberate the entire quantity of the mixed amines by the addition of aqueous sodium hydroxide to the residue, chloroform was used as a solvent for their separation.

Ethylammonium bromide is dissolved by chloroform to the extent of only 0·163 gram in 100 c.c. at 14°, whilst the same volume of chloroform dissolves 42 grams of diethylammonium bromide. By this means, 465 grams of pure ethylammonium bromide and 510 grams of diethylammonium bromide, containing slightly more than 5 per cent. of triethylammonium bromide, were obtained. After the separation of triethylamine (14 grams) by treatment with the requisite proportion of sodium hydroxide, 226 grams of diethylamine, collected at 56—57·5° and dried over potassium hydroxide, were obtained.

(a) *Displacement of Diethylamine by Ethylamine, and of* (b) *Triethylamine by Diethylamine.*

Expt. I.—(*a*) Nine grams of pure ethylamine were added to 12 grams of diethylammonium chloride dissolved in 30 c.c. of alcohol. After an hour, all free amine was removed by distillation. The hydrochloride prepared from the distillate gave Cl = 32·33, whilst $NHEt_2,HCl$ requires Cl = 32·42 per cent. The displacement of the secondary amine from its salt was therefore complete.

Expt. II.—(*b*) Eight grams of pure diethylamine were added to 15 grams of triethylammonium chloride dissolved in 35 c.c. of

alcohol. The mixture was distilled as in the previous experiment. The hydrochloride prepared from the distillate gave Cl = 25·78, whilst NEt_3,HCl requires Cl = 25·81 per cent. The displacement of the tertiary amine by the secondary was therefore complete.

Separation of the Three Amines by Sodium Hydroxide.

Expt. III.—To a solution which contained 13·8 grams of triethylammonium chloride, 11 grams of diethylammonium chloride, and 9 grams of ethylammonium chloride dissolved in 60 c.c. of water, 4 grams of sodium hydroxide were added. The solution was well shaken, and after twenty hours the liberated amine was distilled off.

The hydrochloride prepared from it gave Cl = 26·04, whilst NEt_3,HCl requires Cl = 25·81 per cent. The amine was therefore almost pure triethylamine.

To the remaining solution, when cold, 4 grams of sodium hydroxide were added, and a similar treatment was applied.

The hydrochloride prepared from the liberated amine gave Cl = 34·44, which corresponds with a mixture, in round numbers, of diethylamine = 85 and ethylamine = 15 per cent. The residual solution was directly distilled after a final addition of sodium hydroxide. The hydrochloride prepared from the distillate gave Cl = 41·12; the liberated amine had, therefore, the approximate composition, ethylamine = 75 and diethylamine = 25 per cent. These results indicate that this method of procedure for the separation of the amines may prove useful on a larger scale, and the subject is under investigation in connexion with certain of the higher aliphatic amines.

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[*Received, October 8th,* 1918.]

LXXXIII.—*The Determination of the Molecular Complexity of Liquid Sulphur.*

By ALEX. MITCHELL KELLAS.

SULPHUR has a greater molecular complexity in solution, and also throughout a considerable range of temperature in the gaseous condition, than any other element, and its complexity in the liquid state would therefore seem to be of special interest.

This was recognised by Ramsay and Shields, the pioneers, who, following up a generalisation of Eötvös (*Ann. Phys. Chem.*, 1886, [iii], **27**, 452), made the first series of determinations in connexion with the complexity of liquids, but they stated that no results could be obtained with sulphur, because of its great viscosity (T., 1893, **63**, 1089). After further attempts, Ramsay and Aston made a similar statement as a final conclusion (T., 1894, **65**, 167).

Several years ago, the author, in carrying out the usual lecture experiment of preparing the plastic modification of sulphur, drew the conclusion that viscosity could not be the cause of the failure to obtain definite results, as sulphur is quite mobile from its melting point at 115° up to about 160°, when an abrupt increase of viscosity occurs. This evidently gave a range of about 45° for the determination of the variation of molecular surface energy with temperature, which is larger than that generally used by Ramsay and Shields.

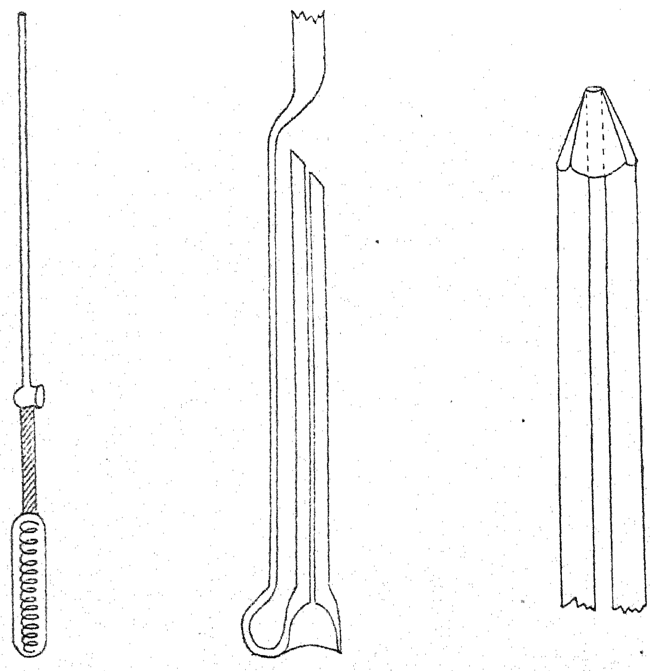
Preliminary experiments showed that it was easy to get liquid sulphur to rise from 4 to 8 cm. in capillary tubes, but also, as was to be expected from the difficulties encountered by such especially careful workers as those above mentioned, that it was impossible to obtain concordant results. As, however, great viscosity—which at this stage was regarded as an almost insuperable factor—was evidently not the cause of the discrepancies observed, the author started a series of experiments in order to determine the actual disturbing agents, and, after great difficulty, was able to devise a course of procedure which allows of the determination of the surface tension of sulphur at any temperature from its melting point to its boiling point (that is, from 115° to 445°).

Derivation of Suitable Apparatus.

It was found necessary completely to modify the apparatus employed by Ramsay and Shields, which consisted of a sealed tube partly surrounded by a vapour jacket. The capillary used by them

was attached to a small cylindrical bulb containing soft iron, which allowed of its being raised into position by means of a magnet (T., 1893, **63**, 1094). It was found possible to work satisfactorily with this apparatus only after jacketing the whole of the reaction tube, an electromagnet being employed to raise the capillary, but, as the latter frequently fractured when the sulphur solidified, thus causing great loss of time, it was eventually decided to alter the apparatus so as to allow of the use of thick-walled capillary tubes.

FIG. 1.



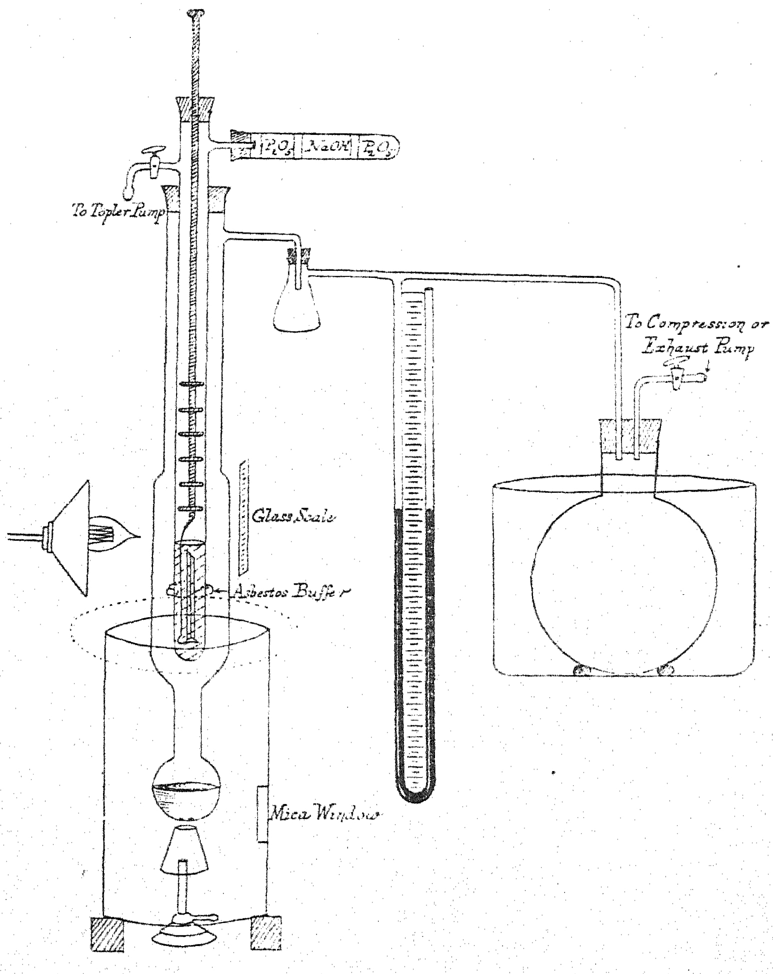
a. b. c.

After experiment, it was found that the stout-walled tubing used for making ethyl chloride jets was suitable, but, being heavy, it was necessary to manipulate it from above. The relationship between the Ramsay and Shields type of capillary and that employed in the work described below is illustrated in Fig. 1. For use in mobile sulphur, it was found convenient to bevel the top of each capillary tube at an angle of 45°, so as to prevent sulphur collecting on irregularities and trickling into the top of the tube during the course of an experiment (Fig. 1, *b*). With viscous

sulphur, however, even this precaution was insufficient, and it was eventually found necessary to bevel each capillary round the top, like a sharpened pencil (Fig. 1, *c*).

The capillary was contained in a long, cylindrical tube closed

FIG. 2.



by a rubber cork, through which passed a stout glass rod attached to the base of the capillary tube, as shown in Fig. 2. The rod was expanded into baffle-disks in its lower portion so as to prevent cooling of the surface of the sulphur by convection currents. A

side-tube provided with a tap allowed of exhaustion of the experimental tube containing the sulphur by means of a Töpler pump. The tube was surrounded by a vapour jacket, and it was eventually found preferable to use a long tube without condenser. The connexion of this jacketing tube to catch-flask, manometer, and air-chamber, which allowed of modification of the boiling point of the liquid used, is illustrated (Fig. 2).

The upper portion of the sulphur and the scale in front were strongly illuminated by an incandescent electric lamp. As the capillary and scale were necessarily a considerable distance apart, a special type of telescope was employed which focussed clearly objects within an exceptional depth of field. The gas in the experimental tube was kept dry by means of a side-tube containing phosphoric oxide and sodium hydroxide, the latter reagent also absorbing sulphur dioxide.

Factors causing Special Difficulty in the Determination of the Surface Tension of Sulphur.

During the long series of experiments carried out while a suitable apparatus was being developed, it was found that concordant results could only be obtained after purification of the sulphur. On investigation of the gases pumped off after boiling, the disturbing agents were evidently sulphur dioxide, sulphuric acid, and hydrogen sulphide, and also perhaps compounds formed from these substances by reaction with sulphur, water being an accessory factor. This agrees with the experience of Moissan (*Ann. chim. Phys.*, 1907, [viii], **10**, 433), Malus (*ibid.*, 1901, [vii], **24**, 491)—who found that fresh gas was evolved even after eighty successive fusions—and other observers.

It was found advisable not to use sulphur which had been exposed to air, as it seemed more difficult to purify, which agrees with the observations of Leonard (*Analyst*, 1901, **26**, 319) and Pollacci (*Boll. chim. farm.*, 1908, **47**, 363), who state that sulphuric acid may be present in quantities up to 0·25 per cent.

Method of Procedure.

At first it was supposed that it was desirable to start with pure sulphur, and the purest crystalline sulphur obtainable was employed. It was later found, however, that if commercial flowers of sulphur were once distilled and the middle fraction used, excellent results could be obtained after purification from sulphur dioxide and the other impurities mentioned above.

Immediately after distillation, the sulphur was poured into the

heated, dry experimental tube. The capillary tube, which had been cleaned by warming with potassium dichromate and sulphuric acid, washed with distilled water, and then heated to about 350° in a small cylindrical electric heater, was inserted in the molten sulphur and the air (or nitrogen) pumped off. The tube was then filled with dry nitrogen and the sulphur boiled for fifteen to twenty minutes; after cooling, the tube was exhausted and left to remain overnight, again filled with dry nitrogen, the sulphur boiled, and, after allowing to cool to about 140°, the capillary was raised from the liquid and the behaviour of the sulphur noted. If the sulphur were pure and the capillary tube clean, any bubbles of gas in the latter which were not spherical would be concave above and below, looking like cylinders with hemispherical ends, and between 120° and 160° would rapidly rise and escape, slight reduction of pressure invariably causing a rapid rise. If, on the contrary, the sulphur or tube were in an unsatisfactory condition, any bubble in the capillary would have more or less flattened menisci, and would not move, even on reducing pressure to a considerable extent.

If unsatisfactory, the process of boiling and exhaustion was repeated, but if the behaviour of the sulphur seemed normal, the tube was surrounded with the vapour of a liquid at a definite temperature and a series of measurements effected. Six determinations were generally carried out for temperatures below 160°, an agreement within 0·01 cm. being required, but in many cases the six readings were identical. At temperatures above 160°, on account of the enormous viscosity, 0·02 cm. was the limit of error, and fewer readings were usually taken, because of the increased length of time required for each experiment.

The substances employed as vapour jackets included glacial acetic acid (b. p. 118°), chlorobenzene (132°), bromobenzene (157°), methyl oxalate (163°), aniline (183°), ethyl benzoate (212°), quinoline (237°), bromonaphthalene (277°), diphenylamine (304°), phenanthrene (340°), and mercury (357°); boiling liquid sulphur (445°) was also used. For substances boiling above 300°, the jacketing tube was wide and had no bulb at the end.

The surface tension apparatus was filled with dry nitrogen during the purification of the sulphur, in order to prevent the formation of sulphur dioxide. Bodenstein and Caro (*Zeitsch. physikal. Chem.*, 1910, **75**, 30) have stated that sulphur oxidises slowly at 150° and rapidly near the temperature of ignition—approximately 245°—which seems to agree with the results observed. It was found to be unsatisfactory to boil the sulphur in a vacuum, as the whole mass was apt to project itself up the tube at about 200°.

Preliminary experiments seem to indicate that ammonia may be used to aid in the purification of sulphur, as might be expected from Smith and Carson's results (*Ber.*, 1902, **35**, 2992).

Determination of Radii of the Capillary Tubes Employed.

In order thoroughly to test the method of working, and also to find out whether the viscosity of sulphur affected the results in narrow tubes, seven capillaries were selected of radii varying from 0·09992 to 0·00895 cm., that is to say, from approximately 2 mm. to 0·18 mm. in diameter. The latter is smaller in bore than any of those employed by Ramsay and Shields or other workers (so far as the author has observed), water rising in it to a height of about 16 cm.

The determinations of bore were effected by means of mercury, the following being the mean values for the respective radii in cm.: (1) 0·09996, (2) 0·0721, (3) 0·05208, (4) 0·03318, (5) 0·02362, (6) 0·01523, (7) 0·00895; number (5) was afterwards found to be slightly oval in section.

Determination of the Density of Sulphur at Different Temperatures.

As trustworthy values of the density of sulphur at different temperatures did not seem to be available, determinations were carried out with three different pieces of apparatus, namely: (1) a large glass dilatometer, with a bulb of capacity 61·287 c.c. at 0°, (2) a small quartz weight-thermometer, the volume of which at 0° was 8·63265 c.c., and (3) a large quartz dilatometer, with a bulb of capacity 56·74 c.c. at 0°.

In the case of the glass dilatometer, the cubical coefficient of expansion of the glass was determined and found to be 0·0000258. The coefficient of expansion of the fused silica ware used was taken as 0·00000177. The table on p. 909 gives a summary of the values obtained.

The agreement of the different series seems fairly satisfactory, but it must be noted that they are not in accord with much of the previously published results. For example, Ossan (*Ann. Phys. Chem.*, 1834, [ii], **31**, 33) gives a density of 1·927 at 115°, Rudge (*Proc. Camb. Phil. Soc.*, 1910, **16**, 59) 1·861 for 133°, and Ramsay (T., 1879, **35**, 471) gives 1·4578 to 1·513 as the density at the boiling point. Space considerations prevent discussion of earlier work, but it might be noted that Kruyt (*Zeitsch. physikal. Chem.*, 1908, **64**, 513) gives a useful bibliography.

The peculiar variation of the coefficient of expansion towards 160° seems to point to an alteration of molecular complexity.

TABLE I.

Density of Sulphur. Collective Table of Results.

Temperature.	Series I. Glass dilatometer (c=calculated).	Series II. Quartz weight-thermometer (c=calculated).	Series III. Quartz dilatometer.	Coefficients of expansion of sulphur calculated from Series III.	
				Temp. range.	Mean coefficients.
115·1°	1·8094	1·8086	1·8084	—	—
122·2	1·8030 c.	1·8028	—	—	—
134·0	1·7921	1·7931	1·7938	115 —134°	0·000430
138·2	1·7877 c.	1·7896 c.	1·7905	134 —138·2	0·000439
145·5	1·7807	1·7839 c.	1·7846	138·2—145·5	0·000465
151·5	1·7761	1·7791 c.	1·7794	145·5—151·5	0·000487
156·9	1·7722 c.	1·7747	1·7747	151·5—156·9	0·000490
158·5	1·7710	1·7739 c.	1·7739	156·9—158·5	0·000282
161·0	1·7704	1·7733 c.	1·7733	158·5—161·0	0·000135
165·0	1·7695 c.	1·7724 c.	1·7724	161·0—165·0	0·000127
171·3	—	1·7705 c.	1·7705	165·0—171·3	0·000170
178·3	1·7652 c.	1·7681 c.	1·7681	171·3—178·3	0·000194
184·0	1·7632	1·7648	1·7651	178·3—184·0	0·000298
210·0	1·7505	1·7510	1·7511	184·0—210·0	0·000308
239·5	1·7307	1·7340	1·7341	210·0—239·5	0·000344
278·5	1·7072	1·7119	1·7097	239·5—278·5	0·000366
357·0	1·6565	1·6563	1·6620	278·5—357	0·000366
445·0	1·5994	1·6047	1·6140	357 —445	0·000338
—	—	Separate experiment	1·6102	357 —445	0·000366

The relationship of density to temperature is well expressed in curve No. 1, which shows clearly the peculiar bend, beginning at about 160°, and resulting in a complete alteration of alignment.

Determination of Surface Tension and Molecular Complexity of Sulphur.

The values for surface tension obtained in the different series of experiments with the seven capillary tubes mentioned above may be most conveniently considered with regard to sulphur between two ranges of temperature:

Part I. Mobile sulphur (S_λ), 115° to 160°.

Part II. Viscous sulphur (S_μ), 160° to 445°.

This division is rendered advisable, because of the extraordinary variations in the viscosity of sulphur. Between 115° and 160°, the viscosity varies only slightly, being given by Rotinjanz (*Zeitsch. physikal. Chem.*, 1908, **62**, 609) as 11 at 120° and 8 at 150°. The viscosity of water at 100° is 0·0028, so that sulphur near its melting point is about 4000 times more viscous than water at its boiling point. At approximately 160°, however, there is a sudden alteration of viscosity, which greatly increases. The augmentation continues up to about 187°, at which temperature Rotinjanz gives the viscosity as 52,000, that is to say, 18,600,000 times greater than water at 100°. Above 190°, the viscosity diminishes, becoming 13,300 at 240° and 74 at the boiling point. It is doubtful, however, whether Rotinjanz was working with pure sulphur.

PART I.

Determination of the Surface Tension, Molecular Surface Energy, and Molecular Complexity of Mobile Sulphur (S_λ), 115—160°.

The results obtained with the capillary tube of approximately 1 mm. bore might be summarised as typical, although presumably not quite so accurate as those determined with narrower tubes. The difficulty of obtaining correct values depends primarily on the impossibility of reading with absolute accuracy the depth of the meniscus at the surface of the liquid in the vessel. The accuracy is generally within 0·01 cm., and the possible error would be less if the capillary tube were aligned so as to be exactly in the centre of the experimental tube.

TABLE II.

Summary of Results of Four Series of Experiments with Capillary Tube No. 3. (Radius, 0·05208 cm.)

Temperature.	116·4°	132°	142·8°	155·6°
Capillary rise in cm.	1·27 : 1·27	1·24 : 1·24	1·225 : 1·225	1·19 : 1·20
	1·27 : 1·27	1·24 : 1·24	1·225 : 1·225	1·19 : 1·19
	1·27 : 1·27	1·24 : 1·24	1·225 : 1·225	1·20 : 1·20
Average capillary rise (cm.)	1·27	1·24	1·225	1·195

From such results, the surface tension can be calculated by working from the general equation usually employed, namely, $\gamma \times 2\pi r \times \cos\theta = \pi r^2 \times (h + r/3) \times (d - d_1) \times g$, where γ is the surface tension, r the radius of the capillary tube, h the capillary rise, $r/3$ the correction for capillary meniscus, d the density of the liquid, d_1 the density of any gas above the liquid, and g the acceleration of gravity. The density of the vapour (d_1) can usually be safely neglected, and since molten sulphur wets glass, $\cos\theta$ may be taken as unity.

As previous workers have assumed that there is a definite contact angle between sulphur and glass, and Rudge (*Proc. Camb. Phil. Soc.*, 1910, **16**, 55) has determined the angle by two methods to be 60°, the author has summarised his reasons for the above conclusion in a separate paper, and need only record here that the behaviour of sulphur during purification seems decisively to negative anything more than a very small contact angle.

In the case of pure fused sulphur, large bubbles of gas in the capillary tube were, as already noted, cylindrical with hemisperical ends, and bubbles of the same diameter as the capillary tube or smaller were apparently spheres, and the contact angle seemed to be zero, the sulphur appearing to wet the glass. In the case of impure sulphur, these relationships did not hold. There seemed to be inconstant contact angles, which might differ considerably in different parts of the same capillary tube, and often approximated to 90°. The diagram on p. 912 (Fig. 3) gives an idea of the nature of the bubbles in the two cases.

The change in form of the bubbles as represented for impure and pure material was invariably accompanied by a great increase of surface tension, which might nearly double or triple in a very short time, and then seemed to remain absolutely constant for a given temperature.

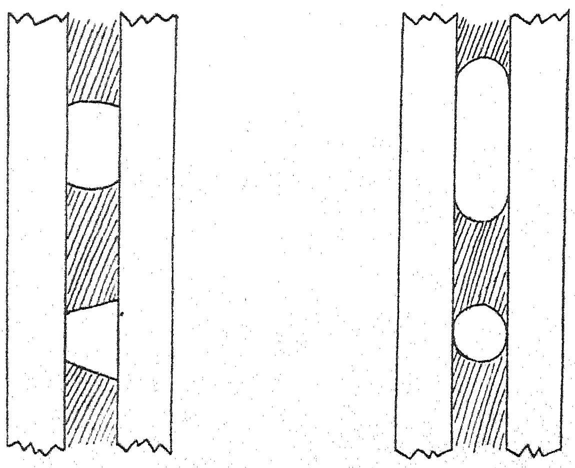
It might also be pointed out that a contact angle of 60° is improbable for two other reasons. In the first place, it would mean multiplying the values of surface tension summarised below

by 2, which would raise the surface tension of sulphur for temperatures above 115° to more than double that of water. In the second place, if the contact angle between sulphur and glass were 60°, the formula deduced from the variation of molecular surface energy with temperature could be represented at S_2, which, in view of the known aggregations of sulphur in the gaseous state and in solution, seems quite inadmissible.

Assuming the angle of contact between sulphur and glass to be zero, the values obtained for surface tension and molecular surface energy are summarised in table III (p. 913).

The mean of the above eleven values for the differential coefficient, K_1, is 1·008, which would give 3·05 as the multiplying

FIG. 3.



Impure sulphur. *Pure sulphur.*

factor for S_2. It must be noted, however, that capillaries Nos. 1 and 2, of diameters 2 and 1·5 mm. approximately, were primarily employed for exploratory purposes in connexion with viscous sulphur, and the results are given in order to show that such capillary tubes are rather wide for accurate work, and the values obtained should not be included in any general averages. Excluding these determinations of K_1, the mean of the remaining nine series is 1·03, which gives 2·96 as the average value for x. Four of these values of K_1 represent, however, comparatively small temperature limits, and what is required here is an average value of K_1 for the whole range of temperature during which sulphur remains mobile after melting, that is to say, for the range

TABLE III.

Mobile Sulphur (S_λ).

Variation of Surface Tension and Molecular Surface Energy with Temperature.

Capillary No.	Temperature.	Series.	Radius of capillary. r	Mean capillary rise in cm. $h + r/3$.	Density of sulphur.	Surface tension in dynes. $\gamma = r/2(h+r/3)dg$.	Molecular surface energy in ergs. $\gamma(Mv)^{\frac{2}{3}}$.	K_1.	Factor for multiplication of S_2. x.
3	116·4°	A	0·05212	1·287(4)	1·807	59·48	642·4	A & B = 1·04	
	132·0	B	0·05213	1·257(4)	1·795	57·72	626·1	A & C = 0·94	3·06
	142·8	C	0·05214	1·242(4)	1·787	56·77	617·7	A & D = 1·04	
	155·6	D	0·05214	1·212(4)	1·776	55·08	601·6		
4	118·8	A	0·03321	2·031	1·805	59·73	645·5	A & B = 1·14	
	144·2	B	0·03322	1·946	1·786	56·65	616·5	A & C = 0·97	2·85
	155·8	C	0·03322	1·928	1·776	55·82	609·6		
5	118·0	A	0·02364	2·933	1·806	61·44	663·6	A & B = 1·05	
	144·6	B	0·02365	2·820	1·785	58·39	635·7	A & C = 1·03	2·91
	155·6	C	0·02365	2·776	1·776	57·22	624·8		
6	121·5	A	0·01523	4·502	1·804	60·67	656·0	A & B = 1·00	3·09
	156·3	B	0·01524	4·284	1·775	56·84	621·2		
7	122·2	A	0·008957	7·695	1·803	60·96	659·4	A & B = 1·07	2·79
	156·9	B	0·00896	7·296	1·775	56·94	622·2		
1	112·0	A	0·10004	0·655	1·810	58·20	627·7	A & B = 0·89	3·68
	158·0	B	0·10008	0·619	1·773	53·89	589·3		
2	117·6	A	0·07216	0·874	1·806	55·89	603·7	A & B = 0·92	3·50
	156·3	B	0·07219	0·827	1·775	51·99	568·0		

115° to 160° inclusive. Average values of molecular complexity for this range can be computed from table IV (p. 915).

These average values for the multiplying factor seem clearly to indicate that it is approximately 3, and therefore a minimum of 95 per cent. of sulphur between 115° and 160° must have a molecular complexity represented by the formula S_6. If the Ramsay and Shield's method of calculation be invalid, then the value of S_6, indicated from above results, would be merely a coincidence, but, if so, it is a remarkable one. The analogy to aggregates of C_6 is obvious.

Part II.—Determination of the Molecular Complexity of Viscous Sulphur. Temperature Range, 160—445°.

It has been already stated that at approximately 160° there is a sudden increase of viscosity, which, according to Rotinjanz, attains a maximum of 52,000 about 190°. The enormous viscosity during the earlier part of the temperature range considered (160° to 220°) causes difficulty in carrying out the experiments. The time required may be considerable; for example, at 183°, even with a tube of 1 mm. diameter, the time taken by the sulphur in falling the last 0·5 cm. was more than three hours, and in the case of the capillary of radius 0·03318 cm., the time taken to fall 0·5 cm. was about twenty hours, and the final readings were taken twenty-five hours after the capillary was raised into position. Presumably time of fall $\propto 1/r^4$, and therefore only tubes above 0·02 cm. radius can be conveniently used for the range 165—220°.

A summary of the results obtained is given in table V (p. 916).

As a preliminary to the consideration of the above results, the variation of surface tension from melting point to boiling point might be represented by a curve in a typical case. Curve No. 2 (Fig. 4, p. 917) shows the relationships graphically, and indicates that the surface tension as such seems not to be affected by the viscosity, and falls in two confluent phases from melting point to boiling point. The remarkable analogy of this curve to that expressing the variation of density with temperature is evident.

As regards the molecular complexity of viscous sulphur, considering the results for capillaries 3 and 4, which, as previously pointed out, are alone valid, the variations of multiplying factor for S_2 are between 6·8 and 14·3, which would correspond with S_{14} and S_{28} or S_{29} respectively. It must be noted, however, that the only high values are between 160° and 183·5°, where the variations of capillary rise are so small as to be within the limits of error, and

TABLE IV.

Mobile Sulphur (S_λ).

Capillary No.	Temperature range.	Variation of capillary rise $h+r/3$.	Variation of surface tension. (Dynes.)	Variation of molecular surface energy. (Ergs.)	K_1.	Factor for multiplication of S_2.
3	116·4—155·6°	1·287—1·212	59·48—55·08	642·4—601·6	1·04	2·91
4	118·8—155·8	2·031—1·928	59·73—55·82	645·5—609·6	0·97	3·23
5	118·0—155·6	2·933—2·776	61·44—57·22	663·6—624·8	1·03	2·96
6	121·5—156·3	4·502—4·284	60·67—56·84	656·0—621·2	1·00	3·09
7	122·2—156·9	7·695—7·296	60·96—56·94	659·4—622·2	1·07	2·79
Average	119·4—156·04	—	60·46—56·38	653·4—615·9	1·02	2·996

TABLE V.

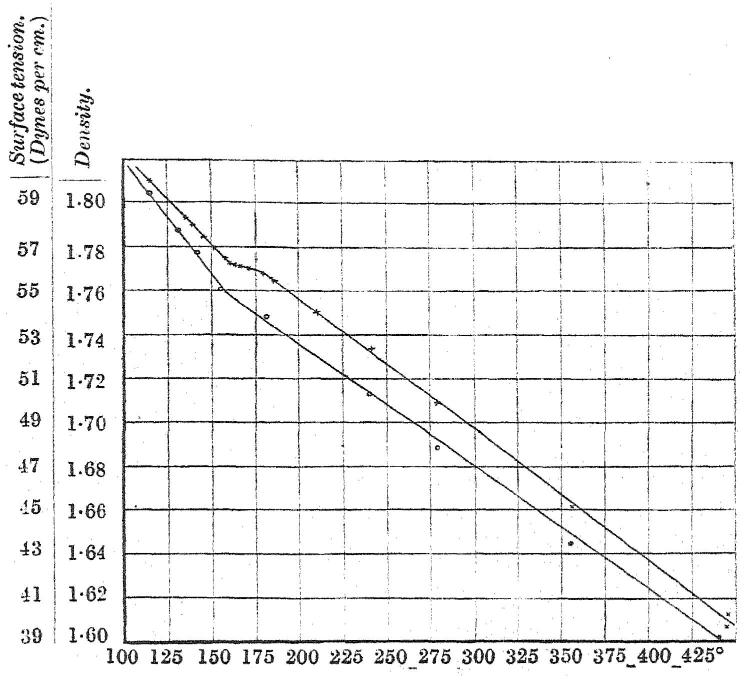
Viscous Sulphur (S_μ).

Variation of Surface Tension and Molecular Surface Energy with Temperature.

Capillary No.	Temperature.	Series.	Radius of capillary r.	Mean capillary rise in cm. $h+r/3$.	Density of sulphur.	Surface tension in dynes $\gamma=r/2(h+r/3)dg$.	Molecular surface energy in ergs $\gamma(Mv)^{\frac{2}{3}}$.	Differential coefficient K_1.	Factor for multiplication of S_2. (x).
1	158°	A	0·10008	0·619	1·773	53·89	589·3	A & B=0·53	8·0
	445·0	B	0·10033	0·473	1·605	37·37	436·7		
2	156·3	A	0·07219	0·827	1·775	51·99	568·0	A & B=0·47	9·59
	445·0	B	0·07236	0·644	1·605	36·69	428·8		
3	155·6	A	0·05214	1·212(4)	1·776	55·08	601·6	A & B=0·36	14·3
	183·5	B	0·05216	1·194	1·765	53·93	591·6		
	239·5	C	0·05218	1·137	1·734	50·47	559·5	A & C=0·5	8·74
	280·0	D	0·05220	1·092	1·710	47·80	535·6	C & D=0·59	6·8
	357·0	E	0·05223	1·027	1·657	43·60	498·9	C & E=0·52	8·2
	445·0	F	0·05227	0·947	1·605	38·97	455·5	C & F=0·51	8·2
4	155·8	A	0·03322	1·928	1·776	55·82	609·6	A & B=0·37	13·7
	183·5	B	0·03323	1·901	1·765	54·69	599·2	A & C=0·50	8·74
	211·0	C	0·03324	1·851	1·751	52·83	582·0		
	241·0	D	0·03324	1·786	1·734	50·51	560·6	A & D=0·57	7·18
	280·0	E	0·03325	1·741	1·710	48·56	544·1	D & E=0·43	10·9
	302·0	F	0·03326	1·706	1·699	47·31	532·1	D & F=0·47	9·59
	357·0	G	0·03328	1·636	1·657	44·27	506·5	D & G=0·47	9·59
	445·0	H	0·03330	1·521	1·605	39·87	466·0	D & H=0·46	9·90

therefore, for sulphur of very great viscosity, it would be inadvisable to lay any stress on values calculated for a short range of temperature. One should nevertheless be able to deduce approximations for long ranges of temperature, and to decide whether the complexity remains nearly unaltered or undergoes distinct variation between 160° and 445°, provided that the Ramsay and Shield's method of calculation can be used for extensive ranges.

FIG. 4.



Upper curve (No. 1) shows the variation of the density of sulphur with temperature.
Lower curve (No. 2) shows the variation of the surface tension with temperature.

A consideration of the values obtained for the following four temperature limits should give sufficient material for deduction of conclusions: (*A*) 160° to 211° and 240°, (*B*) 240—357°, (*C*) 357—445°, (*D*) 160—445°.

The molecular complexity for temperature ranges of 80° or more varies between S_{14} and S_{20}, and for still longer ranges seems to approximate to S_{18}. Although the above results can only be

TABLE VI.

Molecular Complexity of Viscous Sulphur (S_{μ}).

Temperature range.	Capillary No.	Variation of capillary rise in cm.	Variation of molecular surface energy in ergs.	Differential coefficient K_1.	Deduced value of x.	Number of atoms in the sulphur molecule.
155·6—239·5°	3	1·212—1·137	601·6—559·5	0·50	8·74	17–18
155·8—211 }	4	1·928—1·851	609·6—582·0	0·50	8·74	17–18 } 16
155·8—241 }	4	1·928—1·786	609·6—560·6	0·57	7·18	14 }
239·5—357	3	1·137—1·027	559·5—498·9	0·52	8·24	16–17
241 —357	4	1·786—1·636	560·6—506·5	0·47	9·59	19 } 18
211 —357	4	1·851—1·636	582·0—506·5	0·52	8·24	16–17 }
357 —445	3	1·027—0·947	498·9—455·5	0·49	9·00	18
	4	1·636—1·521	506·5—466·0	0·46	9·90	20
160 —445	1	0·618—0·473	587·3—436·7	0·53	8·00	16
	2	0·826—0·644	564·0—428·8	0·47	9·59	19
	3	1·212—0·947	597·6—455·5	0·50	8·74	17–18
	4	1·927—1·521	605·4—466·0	0·49	9·00	18

regarded as first approximations, the similarity of the values obtained seems sufficient to justify the assumption that near 160° sulphur polymerises to form a complex S_{18}, which remains stable up to near the boiling point. The equation representing the transformation in the neighbourhood of 160° would therefore be represented by the symbols $3S_6 \rightleftarrows (S_6)_3$.

The alteration of orientation of the components of the molecule S_6 before and during polymerisation, might explain the peculiar variations of the coefficient of expansion already referred to. It would be easy to represent graphically complexes of S_{18}, which on decomposition near the boiling point might be supposed to give the aggregates S_6, S_8, and S_2, which, according to Preuner and Schupp (*Zeitsch. physikal. Chem.*, 1909, **68**, 129), are present in gaseous sulphur. In particular, their emphasis of the complex S_6 is in accord with the above results for the liquid state.

As regards other important researches, it is evident, however, that the value S_{18} for viscous sulphur (S_μ) cannot be regarded as in agreement with the conclusions of Smith and his collaborators, or others, who regard S_μ as S_6, but the author has no intention of considering fully what might be termed collateral work in this paper, as it would mean undue expansion.

It might perhaps be argued that if polymerisation occurs in the neighbourhood of 160°, then above 190° the proportion of S_μ found by rapid cooling should be constant. This need not necessarily be the case, however. The rapidity of the reverse change might be so great, even in the presence of substances like sulphur dioxide, which Smith has found to act here as a catalytic retarder, that only a small proportion of the complex aggregations could be caught and kept as such by cooling in ice; such aggregates would be in a strained position at the ordinary temperature. The complex molecules at high temperatures would be more easily preserved by rapid cooling, as there would not be time to alter the greater orientation of the atoms in the molecule or of the aggregates of S_6 with regard to each other. What is called plastic sulphur need not, therefore, be so homogeneous as S_{18} in the liquid state, but might consist of aggregates in slightly different conditions of strain. The polymerisation may depend on the lowering of the valency of sulphur with rise of temperature.

Determination of Surface Tension of Sulphur by other Observers.

The results of Zickendraht, Pisati, Capelle, and Rudge might be briefly commented on, but only those obtained by the first-named observer approximate at any temperature to those given above.

Near the melting and boiling points, the values of Zickendraht and the author are nearly concordant, but for viscous sulphur the results are quite different; for example, at 250° Zickendraht (*Ann. Physik*, 1906, [iv], **21**, 141) finds a surface tension of 118 dynes per cm., as against 50 dynes given in table V. It follows that above 160°, Zickendraht's curve showing the variation of surface tension with temperature rises and then falls abruptly in a very peculiar manner.

The results of an earlier observer, Pisati (*Gazzetta*, 1877, **7**, 357), are somewhat similar to those of Zickendraht. His surface-tension curves show a corresponding transverse wave.

A third experimenter, who found that the surface tension of sulphur increased with temperature, was Capelle (*Bull. Soc. chim.*, 1908, [iv], **3**, 764), who obtained a small increase of surface tension between 125° and 142°, and then a rapid increase between 142° and 160°. A few of the results obtained by Capelle, with approximate values calculated from table III, are as follows:

Temperature	125°.	135°.	142°.	152°.	160°.
Capillary rise (Capelle), cm.	2·08	2·08	2·10	2·50	2·74
Calculated values, cm.	5·47	5·39	5·33	5·24	5·18

It is evident that the curves representing these numbers differ both in degree and character.

Another research, where the presence of dissolved substances interfered, has been already referred to in connexion with angles of contact. Rudge (*loc. cit.*) stated that he found no change of surface tension with temperature between 122° and 154°, thus differing entirely from the observers already mentioned. The reason for this statement depends on the experimental error (0·075 cm.) for one temperature being greater than the variation of capillary rise should have been for 30° with the tube used ($r=0·0515$ cm.; compare table III).

The mean value of capillary rise is given as 0·246 cm. at 133°, and the corresponding surface tension 11·56 dynes. The calculated values are 1·27 cm. and 59 dynes per cm. approximately.

The results of the above series of researches indicate conclusively that unless sulphur is nearly pure—the author makes no claim to have prepared absolutely pure sulphur—no definite values can be found for the surface tension.

The critical temperature can be calculated from the above values. $T_c = \frac{\gamma(Mv)^{\frac{2}{3}}}{K_1} + t + 6°$, where t is the temperature of experiment. Two results are obtained, one pertaining to the complex S_6, namely, 766°, and the other corresponding with the aggregate S_{18}, namely, 1390°.

Other Methods of determining Molecular Complexity from Surface Tension Data.

The validity of the Ramsay and Shield's method of calculation as a means of determining molecular weight has been questioned. The values of molecular complexity or of constant (K) obtained from specific formulæ by a few other methods are summarised below.

(1) The specific cohesion (a^2) is 6·8 at 119·4°, instead of 4·3 as previously given, showing that sulphur does not obey Quincke's law. Walden and Dutoit and Moijou give $\dfrac{L_v}{a^2 \times 10^2} = 17{\cdot}9 = K$. The value of K for sulphur at 119·4° is 66, computing L_v as 450.

(2) Walden and Kistiakowsky state that $\dfrac{Ma^2 \times 10^2}{T} = 1{\cdot}162 = K$. M for sulphur by this method is 164·3, indicating a molecular complexity between 5 and 6.

(3) Dutoit and Moijou's empirical relationship between M, pressure (p) at the boiling point, and a^2 indicates for sulphur a molecular complexity of 6 to 7.

(4) Walden states that $\dfrac{Ma^{2\phi}}{T_\phi} = K = 3{\cdot}65$, where T_ϕ is the absolute melting point. Here the formula deduced for the melting point is S_6 (approximately).

(5) Walden gives $\dfrac{ML_\phi}{T_\phi} = K = 13{\cdot}3$. The molecular formula deduced for sulphur would be S_{14}.

(6) Longinèscu's method of calculation, $n = \left(\dfrac{T}{100d}\right)^2$ indicates a formula for S_{12} for the boiling point.

(7) Application of Trouton's rule, and Dunstan's method of calculation from viscosity, seem to point to a high molecular complexity.

All the above methods of calculation indicate considerable association. Whilst the complex S_6 is apparently corroborated in several calculations, yet the Ramsay and Shield's values seem to agree better with the experimental results.

Summary of Conclusions.

(1) Contrary to statements by various observers, the surface tension of liquid sulphur can be determined by means of capillary tubes between the melting point (115°) and the boiling point

(445°). Impurities (especially sulphuric acid, sulphur dioxide, and hydrogen sulphide) must be previously removed.

(2) Sulphur can be purified by distillation and subsequent boiling in dry nitrogen, the gases evolved being pumped off.

(3) *Surface Tension of Mobile Sulphur* (115—160°), S_λ.—A mean value for five capillary tubes gave surface tensions of 60·46 and 56·38 dynes, respectively, for 119·4° and 156°, the corresponding molecular surface energies being 653·4 and 615·9 ergs. The corresponding value of K_1 is 1·02, and the average multiplying factor for S_2 is 2·996 (approximately 3).

(4) The molecular complexity of at least 95 per cent. of mobile sulphur (S_λ) between 115° and 160° is presumably represented by the formula S_6, assuming the validity of the Ramsay and Shield's method of calculation.

(5) The angle of contact of sulphur and glass is taken as zero for reasons assigned.

(6) *Surface Tension of Viscous Sulphur* (160—445°), S_μ.—In disagreement with the results observed by other observers, the surface tension of sulphur falls continuously from the melting point to boiling point, being 48·2 dynes at 280° and 39·4 dynes at 445°.

(7) The molecular complexity alters about 160°, and it might be stated as a first approximation that an endothermic termolecular polymerisation appears to occur near that temperature, $3S_6 \rightleftarrows (S_6)_3$. The aggregate S_{18} seems to be stable up to near the boiling point.

(8) The polymerisation may be due to a tendency of sulphur to lower its valency with rise of temperature, the complex S_6 possessing a residual valency at 160°.

(9) Other methods of calculation of molecular complexity seem to emphasise the aggregate S_6, but the results do not seem to accord with experimental averages so well as those of the Ramsay and Shield's method.

(10) Calculations of critical temperature give two variant values depending on temperature of calculation. Above 160°, the value found is 1390°, corresponding with the complex S_{18}. Below 160°, the inadmissible value of 766° is obtained, corresponding with S_6.

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[*Received, August 28th*, 1918.]

LXXXIV.—*The Freezing Points of Mixtures of Phenol, o-Cresol, m-Cresol, and p-Cresol.*

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IN connexion with some experiments which were undertaken with the object of devising a method for the estimation of the residual phenol in commercial cresylic acids, the authors were led to the consideration of the question of the application of physical methods in the analysis of mixtures of chemically similar substances such as are presented by mixtures of phenol and its homologues.

Although, in general, homologous substances can be separated by fractional distillation, this method is less widely applicable to the separation of isomerides. The tar acids obtained by the distillation of coal consist for the most part of phenol, cresols, and xylenols, and on the basis of the boiling-point differences it is possible to separate the complex mixture of tar acids into fractions which consist for the most part of (1) phenol, (2) *o*-cresol, (3) *m*-cresol and *p*-cresol, (4) xylenols, etc.

In the absence of any large demand for pure cresol fractions, commercial fractionation is usually limited to the production of distillates rich in phenol, from which carbolic crystals may be obtained by crystallisation, and of fractions of higher boiling point containing little phenol and consisting mainly of the three cresols mixed with xylenols. The efficiency of commercial fractionating plants varies very considerably, and although it has been found possible to realise the above series of fractions by the use of suitable fractionating columns, this result has not been generally aimed at and is by no means frequently attained. Mixtures of phenol and its homologues are therefore not only met with in the course of the complex fractionation processes, which are not infrequently regarded as being of the nature of trade secrets, but appear also as the finished products of the tar distiller.

Such products offer an interesting analytical problem, and the authors have had in mind the application of their results to this problem in proceeding to the investigation of the quaternary system having phenol and the three isomeric cresols as its components.

The fact that three of these components are isomerides and homologous with the fourth involves not only a close correspondence in their chemical behaviour, but also a degree of approximation in their physical properties that narrows very considerably

the foundation on which a method for the estimation of the several components in any given mixture may be built up.

Preliminary experiments showed that the freezing-point relations were likely to be of the greatest value in connexion with the analytical problem, and for this reason we have made a detailed examination of the freezing points of the six possible binary combinations, as well as of certain ternary and quaternary mixtures.*

The phenol and cresols used in the investigation were purified by distillation and crystallisation. The phenol was obtained from a commercial sample of carbolic crystals, whilst the *m*-cresol and *p*-cresol were synthetic products. In the case of *o*-cresol, observations were made in part with a purified commercial sample and in part with a substance of synthetic origin. The hygroscopic nature of all four substances demands the utmost care in manipulation, and special precautions were taken to eliminate the last traces of water from all the materials which were used in the freezing-point determinations. For the removal of water, it was found most convenient to heat the substance in a retort for two or three hours, the supply of heat being regulated so that, during this time, from 5 to 10 per cent. of the substance distilled over. The residual liquid was then immediately transferred to a dry, well-stoppered bottle.

The actual data which are recorded in the paper represent the results of observations of the lowest temperatures at which the various mixtures undergo complete liquefaction. Weighed quantities of the components were introduced into glass tubes about 10 cm. long and 1 cm. in diameter, the tubes being carefully sealed with due regard for the necessity of avoiding the introduction of water vapour during the process. A preliminary and approximate determination of the temperature of complete liquefaction was then made, after which the mixture was again solidified and the melting-point tube attached diametrically to a rotating wheel supported in a large water-bath, the temperature of which could be raised very slowly. During this process, the contents of the tube were thoroughly mixed and the temperature at which the

* Since this paper was submitted to the Chemical Society, a communication on the same subject has been published by Fox and Barker (*J. Soc. Chem. Ind.* 1918, **37**, 268). The results obtained by these observers differ very considerably from those recorded in the present paper. The discrepancies would appear to be mainly due to the circumstance that the workers in the Government laboratory have made use of a method for the determination of the freezing points which does not give satisfactory results for many of the mixtures examined, whilst it would seem that the substance they have assumed to be pure *m*-cresol consists of a mixture of about 85 per cent. of *m*-cresol and 15 per cent. of *p*-cresol.

last crystals disappeared was registered. In virtue of the preliminary measurement, it was possible to set the temperature of the water-bath about 1—2° below the temperature to be measured, and to adjust the heat supply so that the temperature rose very slowly. In the case of the mixtures of higher melting point, the temperature of complete liquefaction could be determined in this way within ±0·05°, but at the lowest temperatures the precision of the measurements was not quite so great. The temperatures at which liquefaction is complete correspond with those at which crystallisation of the liquid would begin in the absence of supercooling, and in what follows these temperatures will be referred to as freezing points. It should be mentioned that the crystallisation of certain mixtures does not occur at all readily. This is particularly noticeable in the case of mixtures which contain a large proportion of *m*- or *p*-cresol, and inoculation of the supercooled liquids was occasionally found to be necessary to start crystallisation.

Before proceeding to give the results of our experiments, it may be appropriate to refer to the considerable discrepancies between the values recorded for the melting point of phenol and the cresols in the literature. We have made no attempt to reconcile these divergent numbers, and the freezing-point data recorded in this paper are not put forward with any suggestion that the phenols were absolutely pure, although all reasonable precautions were taken in regard to their purification.

In reference to the tables in which the experimental data are recorded, it may be noted that the composition of those binary mixtures which contain phenol is expressed in terms of both weight percentage and molecular percentage. For mixtures of cresols,

TABLE I.

Phenol and o-Cresol.

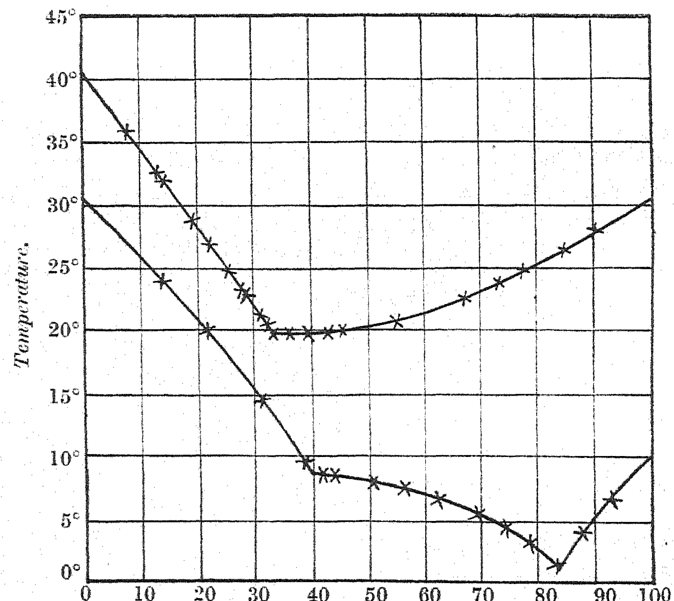
Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40·5°	36·96	33·78	19·7°
9·00	7·93	35·8	39·43	36·16	19·9
14·72	13·06	32·6	42·47	39·12	19·85
15·82	14·06	32·05	46·10	42·68	19·85
21·46	19·22	28·7	48·81	45·35	19·95
24·54	22·06	27·05	58·63	55·23	20·75
28·28	25·55	24·65	69·70	66·69	22·5
30·69	27·82	23·1	75·75	73·11	24·05
31·84	28·9	23·0	80·00	77·69	24·85
34·27	31·21	21·15	86·93	85·11	26·7
34·54	31·47	21·2	91·41	90·25	27·95
36·00	32·87	20·55	100	100	30·45

the two series are, of course, identical. In the freezing-point diagrams which have been constructed from the experimental data, the composition of the mixtures is plotted in terms of the molecular percentage.

The freezing-point curves for mixtures of phenol and *o*-cresol (upper curve in Fig. 1) appear to consist of two branches corre-

FIG. 1.

Phenol and o-*cresol.*
o-*Cresol and* m-*cresol.*



Molecular percentage of o-*cresol (upper curve).*
" " " m-*cresol (lower curve).*

sponding with two series of mixed crystals. Starting from the eutectic, the *o*-cresol branch shows very little change in the freezing point up to about 50 mols. per cent. of *o*-cresol, and for this reason it is scarcely permissible to deny the possibility that there is an intermediate branch corresponding with a compound. There is, however, no clear evidence of compound formation in the case of this particular binary combination.

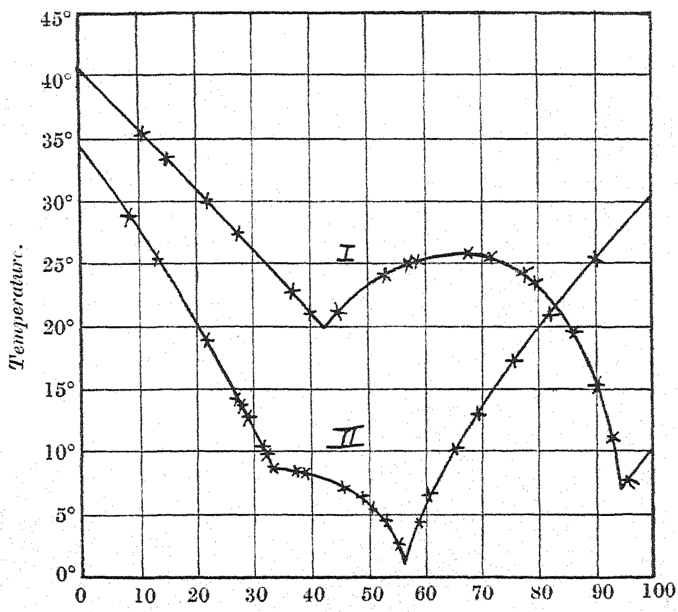
TABLE II.

Phenol and m-*Cresol.*

Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40·5°	61·93	58·59	25·05°
11·73	10·32	35·4	70·25	67·24	25·8
16·26	14·35	33·55	74·36	71·62	25·25
24·23	21·75	29·95	79·72	77·37	24·2
29·83	26·96	27·4	81·94	79·80	23·1
39·98	36·66	22·8	87·54	85·92	19·5
43·44	40·00	21·1	91·52	90·37	15·2
48·37	44·92	21·6	93·72	92·85	11·2
56·54	53·07	24·0	95·89	95·31	7·6
60·40	57·01	24·95	100	100	10·0

FIG. 2.

Phenol and m-*cresol.*
o-*Cresol and* p-*cresol.*



Molecular percentage of m-*cresol* (I).
" " " o-*cresol* (II).

The freezing-point curves for mixtures of phenol and *m*-cresol (see Fig. 2, curve I) are well defined, and show clearly the formation of a compound containing one molecule of phenol in combination with two molecules of *m*-cresol. The flatness of the curve

suggests that the compound is very considerably dissociated in the liquid state. The compound melts at about 25·9°, and the eutectic mixtures which are characteristic of this binary system correspond with 44·8 and 95·2 per cent. by weight of *m*-cresol, the corresponding temperatures being 20·2° and 7·3°.

TABLE III.

Phenol and p-*Cresol.*

Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40·5°	53·90	50·45	0·1°
12·50	11·06	32·35	57·50	54·06	0·75
20·04	18·00	26·8	60·55	57·17	0·8
24·50	22·02	23·9	62·88	59·59	4·65
29·07	26·27	19·6	68·18	65·10	10·0
33·76	30·75	15·25	76·27	73·67	16·55
38·21	34·92	11·05	79·60	77·25	19·5
42·45	39·07	6·65	83·63	81·64	22·3
43·22	39·83	4·9	84·17	82·23	22·75
45·11	41·70	2·5	91·47	90·32	28·15
47·37	43·93	0·2	96·06	95·49	31·2
49·77	46·33	−1·4	100	100	34·15

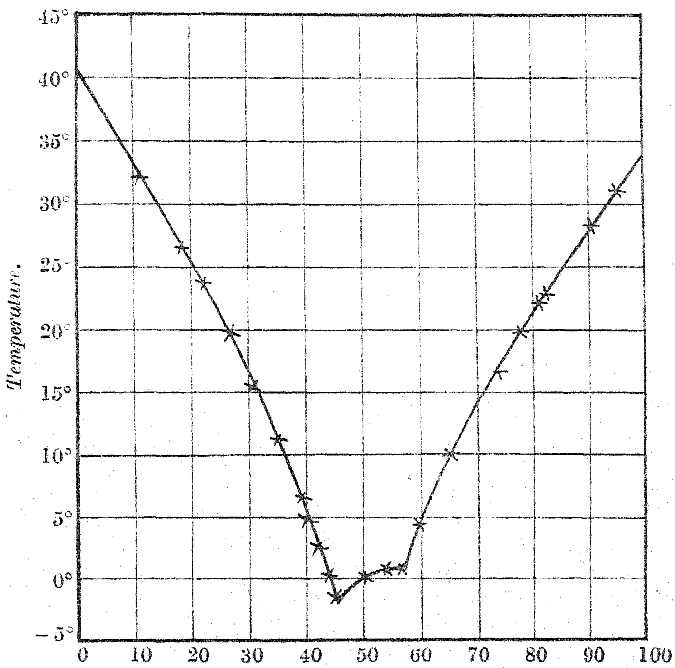
The curve system for mixtures of phenol and *p*-cresol (Fig. 3) affords evidence of the formation of a compound which crystallises at low temperatures from a limited range of mixtures. Although the freezing-point curve corresponding with the compound has not been determined with the desired precision, it seems probable that the compound contains one molecule of phenol in combination with two molecules of *p*-cresol, and that the corresponding curve is terminated by a eutectic point on the phenol side and by a transition point on the *p*-cresol side. The compound crystallises only from mixtures which contain phenol in excess of that proportion which is characteristic of the compound itself.

The freezing points of mixtures of phenol and *p*-cresol have been previously investigated by Lunge and Zschokke (*Chem. Ind.*, 1885, 6; Lunge, "Coal Tar and Ammonia," 5th edition, Part I, 1916, 277), and from the results obtained, these authors drew the conclusion that there are only two curves which meet in a eutectic point. Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842), without recording their experimental data, claim to have obtained the same result. In regard to this discrepancy, we would point out that our experimental numbers differ very widely from those of Lunge and Zschokke in the case of mixtures which contain an excess of phenol, and there can be no doubt whatever that the measurements of these authors involve errors of large magnitude.

On the other hand, if the data recorded by Lunge and Zschokke are plotted, the distribution of the points is such as to suggest the existence of an intermediate freezing-point curve, although these

FIG. 3.

Phenol and p-cresol.



authors interpreted these data in favour of a curve system consisting of two branches.

TABLE IV.

o-*Cresol and* m-*Cresol.*

Per cent. *m*-cresol.	F. p.	Per cent. *m*-cresol.	F. p.
0	30·45°	62·80	6·5°
13·74	23·95	69·28	5·8
21·69	20·00	74·39	4·6
31·31	14·6	78·69	3·6
38·75	9·4	83·25	1·7
41·64	8·5	88·02	4·3
43·68	8·3	93·39	6·6
50·64	7·9	100	10·0
56·14	7·6		

The diagrammatic representation of the data obtained for mixtures of *o*-cresol and *m*-cresol (lower curve in Fig. 1) points to the formation of a compound containing two molecules of *o*-cresol in combination with one molecule of *m*-cresol. The curve corresponding with the compound ends on the *o*-cresol side in a transition point at 8·5° and about 40 per cent. of *m*-cresol, whilst on the *m*-cresol side the compound curve terminates in the eutectic at 1·5° and 83·7 per cent. of *m*-cresol.

TABLE V.

o-*Cresol and* p-*Cresol.*

Per cent. *p*-cresol.	F. p.	Per cent. *p*-cresol.	F. p.
0	30·45°	61·02	8·5°
9·94	25·3	62·76	8·6
17·91	20·85	66·70	8·7
24·27	17·2	67·88	9·8
30·40	13·0	68·40	10·3
34·91	10·1	70·99	12·6
39·36	6·5	71·84	13·6
41·42	4·4	72·60	14·1
44·41	2·5	78·44	18·9
47·11	4·6	87·00	25·3
49·42	5·5	91·70	28·45
51·17	6·4	100	34·15
54·04	7·0		

According to the diagram showing the relation between the freezing points of mixtures of *o*-cresol and *p*-cresol (see Fig. 2, curve II), it is evident that chemical combination occurs with the formation of a compound containing one molecule of *o*-cresol and two molecules of *p*-cresol. The curve for the compound terminates on the *o*-cresol side in a eutectic point at 1·2° and 43·7 per cent. of *p*-cresol, and intersects the *p*-cresol curve at a point which corresponds very nearly with the composition of the compound. The plot of the experimental results does not permit of any definite statement with respect to the nature of the point of intersection,

TABLE VI.

m-*Cresol and* p-*Cresol.*

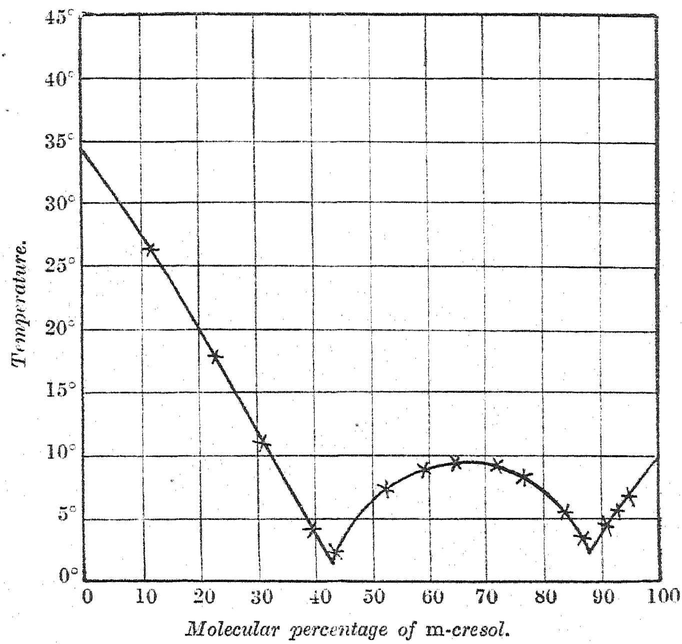
Per cent. *p*-cresol.	F. p.	Per cent. *p*-cresol.	F. p.
0	10·0°	41·22	8·8°
5·10	6·7	47·99	7·4
6·74	5·4	56·39	2·4
9·13	4·4	60·38	4·2
13·40	3·5	68·41	11·0
16·50	5·6	77·03	18·0
23·48	8·2	88·39	26·5
28·41	9·2	100	34·15
35·71	9·5		

but it is evident that the melting point of the compound is approximately 8·7°.

The freezing-point diagram for this pair of isomerides (Fig. 4) shows clearly the formation of a compound containing two molecules of *m*-cresol and one molecule of *p*-cresol. The relations exhibited resemble closely those which are shown by mixtures of *m*-cresol and phenol, and the compounds formed in the two cases contain the same proportion of *m*-cresol. The compound curve is terminated on the *m*-cresol side by the eutectic at 2·0° and 12·0

FIG. 4.

m-*Cresol and* p-*cresol.*



per cent. of *p*-cresol, and on the *p*-cresol side by the eutectic at 1·2° and 57·0 per cent. of *p*-cresol.

Although the diagrams which have been described afford a general survey of the equilibrium relations in the several binary systems, it is of interest to compare the changes which are produced in the freezing point of each of the four components when the three others are separately added. In making this comparison, it is more convenient to express the composition in terms of weight percentage. The advantage attaching to the weight percentage freezing-point curves is obvious when it comes to the application

of the freezing-point relations, and it need only be pointed out that when phenol is one of the two components, the curves in question will be slightly different from those shown in Figs. 1, 2, and 3.

Depression of the Freezing Point of Phenol by the Addition of o-, m-, *and* p-*Cresol.*

The depression of the freezing point of phenol produced by a given weight of cresol varies considerably according to the relative position of the methyl and hydroxyl groups in the cresol molecule. This is evident from the numbers in the following table (VII), which gives the freezing points of phenol–cresol mixtures containing 10, 15, 20, 25, 30, 35, and 40 per cent. by weight of *o*-cresol, *m*-cresol, and *p*-cresol respectively. The table shows that *m*-cresol produces the least effect and *p*-cresol the greatest.

According to Eykman's observations (*Zeitsch. physikal. Chem.*, 1899, **4**, 497), the molecular value of the depression of the freezing point of phenol which is produced by the addition of *p*-cresol is appreciably less than the value calculated from van't Hoff's formula, and also less than the average depression for a large number of different substances. It would seem, therefore, that solid solutions in phenol are formed by all three cresols, although the tendency to form these solutions increases considerably in passing from *p*-cresol to *o*-cresol and from *o*-cresol to *m*-cresol. On account of the divergence between the three freezing-point curves, it is impossible to make use of the freezing point of a phenol–cresol mixture for the estimation of the proportion of phenol present unless the nature of the admixed cresol is known.

The table in question also shows the results which have been obtained in the investigation of the effects produced by the addition of mixed cresols, and more particularly of mixed cresols containing only *m*-cresol and *p*-cresol. The numbers have been interpolated from curves representing the actual freezing-point data.

TABLE VII.

Freezing Points of Phenol–Cresol Mixtures.

Nature of added cresol.	10 per cent. cresol.	15 per cent. cresol.	20 per cent. cresol.	25 per cent. cresol.	30 per cent. cresol.	35 per cent. cresol.	40 per cent. cresol.
m-Cresol	36·2°	34·0°	31·8°	29·6°	27·3°	25·0°	22·6°
o-Cresol	35·1	32·4	29·6	26·75	23·75	—	—
p-Cresol	33·8	30·4	26·8	23·1	19·0	14·4	9·5
m- + *p*-Cresol = 2 : 1	35·1	32·4	29·6	26·75	23·75	20·75	17·5
m- + *p*-Cresol = 1 : 1	34·7	31·75	28·7	25·5	22·1	18·6	14·9
m- + *p*-Cresol = 1 : 2	34·3	31·2	28·0	24·6	20·9	17·1	13·0
o- + *m*- + *p*-Cresol = 1 : 1 : 1	34·9	32·1	29·1	26·1	23·0	19·9	16·6

With regard to the change produced in the freezing point of phenol by the addition of a mixture of *m*-cresol and *p*-cresol, the table shows that the freezing point falls continuously as the proportion of the para-isomeride in the mixed cresol increases. The observed freezing points are, however, lower than those calculated from the separate effects produced by *m*-cresol and *p*-cresol on the basis of the simple mixture rule. For mixtures which contain a fixed proportion of phenol (60 to 80 per cent.), the variation of the freezing point with the composition of the admixed cresol is of such magnitude that the freezing point of such mixtures may be conveniently utilised in the estimation of *m*-cresol and *p*-cresol in their mixtures and in the evaluation of commercial "meta-cresol."

The change in the freezing point of phenol which is produced by the addition of a mixture of *o*-, *m*-, and *p*-cresol in equal proportions is slightly greater than that produced by the same quantity of *o*-cresol. The effect produced by *o*-cresol is within very narrow limits the same as that produced by a mixture of *m*-cresol and *p*-cresol in the proportion 2 : 1.

Lowering of the Freezing Point of o-*Cresol on the Addition of Phenol,* m-*Cresol, and* p-*Cresol.*

The weight percentage freezing-point curves show that equal quantities of phenol, *m*-cresol, and *p*-cresol lower the freezing point of *o*-cresol to different extents. The largest depression is produced by *p*-cresol, but the influence of *m*-cresol is not very different. On the other hand, the depression produced by the same weight of phenol is very much smaller, and this difference is probably due to the greater tendency of phenol to crystallise out with the *o*-cresol in the form of solid solutions. Table VIII affords a comparison of the freezing points of mixtures which contain equal weights of phenol, *m*-cresol, and *p*-cresol respectively; the numbers have been obtained by extrapolation from the corresponding curves.

TABLE VIII.

	Weight per cent. of solute.		
Nature of solute.	10 per cent.	20 per cent.	30 per cent.
Phenol	27·6°	24·95°	22·6°
m-Cresol	25·8	20·8	15·4
p-Cresol	25·2	19·6	13·2

Lowering of the Freezing Point of m-*Cresol on the Addition of Phenol,* o-*Cresol, and* p-*Cresol.*

The three curves which represent the depression of the freezing point of *m*-cresol on the addition of phenol, *o*-cresol, and *p*-cresol are characterised by their relatively short extension In the case where phenol is added, the limit is reached when the mixture contains less than 5 per cent. of phenol. In consequence of the small amount of pure *m*-cresol at our disposal and of the difficulty in measuring the freezing points with the requisite accuracy, these curves have not been examined in any detail. Although, therefore, further observations are required in order to determine the relative slopes of the curves, it seems probable that the freezing point of *m*-cresol is depressed to a greater extent by *p*-cresol than by the same quantity of *o*-cresol.

Lowering of the Freezing Point of p-*Cresol on the Addition of Phenol,* o-*Cresol, and* m-*Cresol.*

The behaviour of *p*-cresol as solvent is of particular interest by reason of the fact that its freezing point is depressed to almost exactly the same extent by equal weights of either phenol, *o*-cresol, or *m*-cresol. In this respect, *p*-cresol differs notably from phenol and *o*-cresol. The three freezing-point curves are, moreover, of wide range, the shortest extending to a point at which the temperature is about 26° below the freezing point of pure *p*-cresol. Since the weight percentage freezing-point curves are approximately identical, it follows that the freezing point of a mixture containing an excess of *p*-cresol affords a direct measure of the proportion of *p*-cresol in the mixture.

Summary and Discussion.

The freezing-point relations which have been described in the preceding pages show that there is considerable diversity in the behaviour of the several binary combinations when the liquid mixtures are allowed to crystallise.

In the case of binary mixtures which contain phenol in excess, the behaviour of the three cresols suggests that the tendency to crystallise out with the phenol increases markedly in the order *p*-cresol, *o*-cresol, *m*-cresol. With *p*-cresol as solvent, there is, on the other hand, very little difference in the behaviour of the three solutes phenol, *o*-cresol, and *m*-cresol, and although the experiments do not afford any quantitative information, it seems prob-

able that solid solution formation is very limited when mixtures containing an excess of *p*-cresol are allowed to crystallise. The position of *o*-cresol as solvent is intermediate, in that *m*-cresol and *p*-cresol as solutes show only a limited tendency to crystallise out with the *o*-cresol, whilst phenol separates out with the *o*-cresol in considerable quantities.

The fact that five out of the six binary systems afford evidence of the formation of definite compounds is rather remarkable in view of the close chemical similarity of the components. According to results obtained by Kendall and his co-workers (compare *J. Amer. Chem. Soc.*, 1917, **39**, 2303, and previous papers) in the investigation of the formation of additive compounds of various types of organic substances, it would appear that the formation of such compounds is in large measure determined by the difference in the basic or acid character of the components. The greater this difference, the greater the tendency to form additive compounds and the more stable the compounds which are formed. In the group of substances which we have examined, the differences in question are extremely small, and the relations disclosed by the freezing-point diagrams are consequently not in accord with what would have been anticipated on the basis of the views advocated by Kendall.

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[*Received, August 27th*, 1918.]

LXXXV.—*The Estimation of Phenol and the Three Isomeric Cresols in Mixtures of these Substances.*

By HARRY MEDFORTH DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD.

IN the preceding paper, the authors have described the freezing-point diagrams for the six possible pairs of substances which correspond with the quaternary system phenol, *o*-cresol, *m*-cresol, and *p*-cresol. The relations exhibited by the diagrams suggest that the determination of the freezing point may prove to be of considerable value in the analysis of mixtures of these substances.

The value of the freezing-point measurement has long been recognised in connexion with the grading of commercial carbolic acids. It forms the basis of the widely used empirical method

described by Lowe for the standardisation and specification of coal-tar carbolics, and this method may, in fact, be used for the approximate estimation of phenol in commercial products which contain a sufficiently large proportion of phenol.

In recent years, the question of the estimation of phenol in tar acids has received considerable attention. Methods depending on freezing-point observations have been described by Weiss (*J. Franklin Inst.*, 1912, 683; compare also *J. Ind. Eng. Chem.*, 1917, **9**, 569) and by Masse and Leroux (*Compt. rend.*, 1916, **163**, 361), and a distinct advance in the application of the freezing-point method to the estimation of phenol in commercial carbolic and cresylic acids has been made by Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842; compare also *ibid.*, 1918, **37**, 265), whose method involves the production by distillation of a mixture in which the phenol is associated only with *o*-cresol

In attempting to determine completely the composition of mixtures containing phenol and the three cresols, we are concerned with a problem which is much wider in scope than that presented by the estimation of the phenol content. The four substances concerned give rise to six groups of binary mixtures, four groups of ternary mixtures, and the quaternary mixture in which all four are present. Theoretically, these various groups are of equal interest and importance, but a distinction can readily be made when the practice of the tar industry is considered. The separation of the homologues is based on differences in boiling point, and fractional distillation tends to eliminate the constituents in the order of their respective boiling points. For the four substances with which we are concerned, the approximate boiling points are: phenol 182°, *o*-cresol 192°, *m*-cresol 202°, *p*-cresol 202°. According to these data, it is evident that a binary mixture such as phenol and *m*-cresol, or a ternary mixture such as phenol, *o*-cresol, and *p*-cresol, will never be met with in works practice, and in this way it is possible to reduce the eleven possible groups of mixtures down to four which are of practical importance. These consist of the two binary series of mixtures with phenol and *o*-cresol, or *m*-cresol and *p*-cresol as components, the ternary series containing *o*-cresol, *m*-cresol, and *p*-cresol, and the quaternary series.

In reference to the application of physical methods in the analysis of liquid mixtures, it may be noted that binary mixtures present little difficulty. In the case of ternary mixtures, physical data are much more difficult to interpret, but under certain conditions it is possible to arrive at the composition of such mixtures without resort to chemical analysis. The application of chemical methods of separation would seem to be almost a necessity when

mixtures of greater complexity have to be dealt with. In the case of the four substances with which we are immediately concerned, the chemical properties are so similar that it has not yet been possible to devise a chemical method which is applicable to the general case of the quaternary mixture, and for this reason the attempt to solve the problem by the application of physical methods is of particular interest.

Before proceeding to describe the methods which we have devised for the analysis of the four groups of mixtures referred to above, it will be convenient to tabulate the values of certain physical properties.

TABLE I.

Property.	Phenol.	*o*-Cresol.	*m*-Cresol.	*p*-Cresol.
Density D_4^{25}	1·0710	1·0415	1·0295	1·0295
Freezing point	41·0°	30·45°	10·0°	34·15°
Boiling point (760 mm.)	182·2°	191·8°	202·1°	202·5°
Refractive index N_D (40°)	—	1·53719	1·53322	1·53187
Viscosity η (25°)	0·0883	0·0762	0·1240	0·1413
Solubility in water (20°), per cent.	8·5	2·8	2·3	2·0
Ionisation constant $K \cdot 10^{10}$ (25°)	1·15	0·63	0·98	0·67

The densities and freezing points given in the table are our own values, which in some cases differ appreciably from numbers recorded in the literature. For instance, the freezing point of *m*-cresol is about 6° higher than the values previously given. The boiling points and refractive indices are taken from Fox and Barker's paper (*loc. cit.*), the viscosities are values interpolated from Bramley's measurements (T., 1916, **109**, 434), the solubilities are those recorded by Sidgwick, Spurrell, and Davies (T., 1915, **107**, 1202), and the ionisation constants those given by Boyd (T., 1915, **107**, 1538). The differences shown by the cresols are not very large, but in certain cases they are sufficient to afford preliminary information of considerable value.

In proceeding to consider the four technically important groups of mixtures, it will be convenient to deal in the first place with the binary mixtures.

I. *Analysis of Mixtures of Phenol and* o-*Cresol.*

The densities of phenol and *o*-cresol are sufficiently different to permit of the density being used in the evaluation of mixtures of these substances. Although admixture is accompanied by a slight contraction, which amounts to about 0·033 per cent. in the case of the 50 per cent. mixture, the composition of any mixture may be calculated from its density by application of the simple mix-

ture rule. On account of the divergent values which are recorded in the literature for the density of *o*-cresol, it does not at present seem possible, however, to recommend the density for this purpose except as a means of providing preliminary information. In the circumstances, more satisfactory results would seem to be obtained by the freezing-point method.

By inspection of the freezing-point curves for mixtures of phenol and *o*-cresol, it will be observed that the slope of the phenol branch is much steeper than that of the *o*-cresol branch, and also that the change in freezing point is very small for a certain range of mixtures. The greater slope of the phenol curve signifies a greater sensitiveness of the freezing point to change in composition when the mixture contains an excess of phenol, and the flat portion indicates that the composition of mixtures which contain more than about 30 and less than about 70 per cent. of *o*-cresol cannot be estimated directly by the freezing-point method.

Having regard to these facts, the examination of an unknown mixture, X, may advantageously begin with the measurement of its density. If the mixture contains phenol or *o*-cresol in considerable excess ($D^{25}_{4} > 1{\cdot}061$ or $< 1{\cdot}050$), the composition may be deduced directly from the freezing point of X, the phenol branch being used for the mixtures of higher density and the *o*-cresol branch for those falling within the lower range. If the density lies between the above limits, X should be mixed with a known proportion of standard phenol (m. p. 40·5°), so as to raise the density of the resulting mixture, Y, above 1·061. The freezing point of Y is then measured. Assuming that a parts of X are mixed with $100-a$ parts of phenol, and that this mixture, Y, contains, according to the freezing-point measurement, y per cent. of phenol, then the percentage of phenol in X is given by the equation $x=(y-100+a)100/a$.

In table II we give the freezing points of mixtures rich in phenol or in *o*-cresol from which the composition of any such mixture may be derived.

TABLE II.

Weight per cent. phenol	**100**	**95**	**90**	**85**	**80**	**75**	**70**
Freezing point	**40·5°**	**37·9°**	**35·2°**	**32·4°**	**29·5°**	**26·5°**	**23·4°**
Weight per cent. *o*-cresol	**100**	**95**	**90**	**85**	**80**	**75**	**70**
Freezing point	**30·45°**	**29·0°**	**27·6°**	**26·25°**	**24·95°**	**23·7°**	**22·6°**

Example.—$X=48{\cdot}0$ per cent. phenol, 52·0 per cent. *o*-cresol.

$Y=40{\cdot}4$ per cent. $X+59{\cdot}6$ per cent. phenol, freezing point 28·8°. Per cent. phenol in $Y=78{\cdot}7$, whence per cent. phenol in $X=47{\cdot}3$.

II. *Analysis of Mixtures of* m-*Cresol and* p-*Cresol.*

By reference to table I, it is evident that the differences between the physical properties of liquid *m*- and *p*-cresol are very small. Greater differences are found in their chemical behaviour, and Raschig (*Zeitsch. angew. Chem.*, 1900, **14**, 759) has described a nitration method which is said to afford a means of estimating *m*-cresol in mixtures which contain all three cresols The claim that the yield of trinitro-*m*-cresol is independent of the proportions of *o*-, *m*-, and *p*-cresol in the mixture is not supported by the results which we have obtained.

A further chemical method, described by Ditz and Cedivoda (*Zeitsch. angew. Chem.*, 1899, **13**, 873, 879), is based on the greater bromine absorbing capacity of *m*-cresol as compared with that of *o*-cresol and *p*-cresol, but it does not seem to have been established that trustworthy results can be obtained in this way.

If the freezing-point diagram for mixtures of *m*-cresol and *p*-cresol (Fig. 4 of preceding paper) is examined, it will be observed that the *p*-cresol curve extends over a considerable range, and that the curve is such that small changes in composition have a considerable influence on the freezing point. The *p*-cresol curve is accordingly well adapted for use in the estimation of *p*-cresol in mixtures of *m*- and *p*-cresol. In applying the freezing-point method, the mixture X may advantageously be mixed with a known proportion of pure *p*-cresol and the freezing point of the resulting mixture, Y, determined. The ratio X : *p*-cresol = 1 : 2 will be found most generally convenient. From the freezing point, the percentage of *p*-cresol may then be read off from the curve which corresponds with the numbers in table III, and the percentage of *p*-cresol in X calculated as previously described.

TABLE III.

Freezing Points of p-*Cresol in Admixture with* o-*Cresol*, m-*Cresol*, *or Phenol.*

p-Cresol, per cent. ...	100	95	90	85	80	75	70	65
Freezing point.........	34·15°	30·7°	27·2°	23·6°	20·0°	16·3°	12·3°	7·8°

If the freezing point of mixture Y is higher than about 25°, X may be mixed with a smaller proportion of *p*-cresol, and the freezing-point measurement repeated.

An alternative freezing-point method for the estimation of the proportions of *m*-cresol and *p*-cresol in a mixture of the two has already been referred to in the preceding paper. In the applica-

tion of this method, the mixture X should be mixed with standard phenol to give a ternary mixture which contains 60 to 70 per cent. of phenol. The freezing-point of this phenol–cresol mixture is determined, and since the temperature varies considerably when the percentage of phenol in the mixture is kept constant and the ratio of *m*-cresol to *p*-cresol in the admixed cresol is altered, it follows that the composition of the mixture X may be deduced from the observed freezing point. Table IV gives the freezing points of mixtures containing 60, 65, and 70 per cent. of phenol respectively, the composition of the admixed cresol being indicated by the horizontal series of figures, ranging from 0 to 100 per cent. of *m*-cresol.

TABLE IV.

Freezing Points of Mixtures of Phenol, m-*Cresol, and* p-*Cresol.*

Per cent. phenol in ternary mixture.	Per cent. *m*-cresol in mixture of *m*- and *p*-cresol.										
	0	10	20	30	40	50	60	70	80	90	100
60	9·5°	10·5°	11·6°	12·7°	13·8°	15·0°	16·4°	17·8°	19·3°	21·0°	23·6°
65	14·4	15·1	15·9	16·8	17·8	18·8	19·9	21·0	22·2	23·5	25·0
70	19·0	19·5	20·1	20·7	21·4	22·1	22·9	23·8	24·8	26·0	27·3

Although this method is not so sensitive as the method of analysis which is based on the use of the *p*-cresol freezing-point curve, it has been found to be quite trustworthy.

Example.—X = mixture of *m*-cresol and *p*-cresol.

First Method.—$Y = 30·6$ per cent. $X + 69·4$ per cent. *p*-cresol, freezing point 16·5°, from which per cent. *p*-cresol in $Y = 75·3$ and in $X = 19·3$.

$Y' = 37·8$ per cent. $X + 62·2$ per cent. *p*-cresol, freezing point 12·3°, from which per cent. *p*-cresol in $Y' = 70·0$ and in $X = 20·6$.

Second Method.—$Z = 33·4$ per cent. $X + 66·6$ per cent. phenol, freeing point 23·35°, from which, by reference to curves constructed from the numbers in table IV (see above) and the data contained in table VII of the preceding paper, per cent. *p*-cresol in $X = 19$.

III. *Analysis of Ternary Mixtures containing* o-*Cresol,* m-*Cresol, and* p-*Cresol.*

Since *m*-cresol and *p*-cresol have the same density, which is appreciably less than the density of *o*-cresol, and the volume changes which occur on mixing are very small, the measurement

of the density affords a rough estimate of the proportion of *o*-cresol in the ternary mixture under examination. Not much information can be obtained from the investigation of other physical properties of a ternary liquid mixture, but the nitration and bromination methods will afford some indication of the proportion of *m*-cresol.

A ternary mixture of the cresols may, however, be completely analysed, without resort to chemical methods, by means of suitable freezing-point measurements. The method depends on the fact that equal weights of *o*-cresol and *m*-cresol depress the freezing point of *p*-cresol to the same extent, and on the further fact that equal weights of *m*-cresol and *p*-cresol depress the freezing point of *o*-cresol to nearly the same extent. In the application of the method, the unknown mixture *X* is mixed with a known quantity of pure *p*-cresol, giving a mixture, *Y*, the freezing point of which is determined. From this, the percentage of *p*-cresol in *Y*, and hence in *X*, can be obtained from the freezing-point curve corresponding with the numbers already given in table III.

Similarly, *X* is mixed with a known proportion of pure *o*-cresol, giving a mixture, *Z*, the freezing point of which is also measured. From this, the percentage of *o*-cresol in *Z*, and hence in *X*, may be derived from the freezing points recorded in table V. These temperatures correspond with a freezing-point curve which lies between the curves representing the changes produced in the freezing point of *o*-cresol on the addition of *m*-cresol and *p*-cresol respectively.

TABLE V.

Freezing Points of o-*Cresol in Admixture with* m- *and* p-*Cresol.*

o-Cresol, per cent. ...	100	95	90	85	80	75	70	65
Freezing point.........	30·45°	28·05°	25·6°	23·1°	20·4°	17·5°	14·4°	11·0°

The proportions of *p*-cresol and *o*-cresol most suitable for the production of the mixtures *Y* and *Z* are indicated, if necessary, by preliminary freezing-point observations on mixtures containing one part of *X* and two parts of *p*-cresol and *o*-cresol respectively.

Example.—*X* = 42·5 per cent. *o*-cresol, 46·0 per cent. *m*-cresol, 11·5 per cent. *p*-cresol.

(*a*) Estimation of *p*-cresol.

Y = 23·5 per cent. *X* + 76·5 per cent. *p*-cresol, freezing point 19·5°, whence per cent. *p*-cresol in *Y* = 79·3 and in *X* = 11·9.

Y′ = 29·4 per cent. *X* + 70·6 per cent. *p*-cresol, freezing point 15·1°, whence per cent. *p*-cresol in *Y′* = 73·5 and in *X* = 10·0.

(*b*) Estimation of *o*-cresol.

$Z = 26 \cdot 1$ per cent. $X + 73 \cdot 9$ per cent. *o*-cresol, freezing point $23 \cdot 0^\circ$, whence per cent. *o*-cresol in $Z = 84 \cdot 8$ and in $X = 41 \cdot 8$.
$Z' = 42 \cdot 3$ per cent. $X + 57 \cdot 7$ per cent. *o*-cresol, freezing point $17 \cdot 6$, whence per cent. *o*-cresol in $Z' = 75 \cdot 2$ and in $X = 41 \cdot 4$.

Taking the mean values found for *p*-cresol and *o*-cresol, the freezing-point method of analysis gives $X = 41 \cdot 6$ per cent. *o*-cresol, 47·4 per cent. *m*-cresol, 11·0 per cent. *p*-cresol.

IV. *Analysis of Quaternary Mixtures containing Phenol,* o-*Cresol,* m-*Cresol, and* p-*Cresol.*

The determination of the composition of a quaternary mixture involves the assignment of definite values to each of three independent variables, and in these circumstances the physical properties of the liquid mixtures afford comparatively little information with regard to the proportions of the components except in certain special cases. At the same time, an approximate idea of the nature of the mixture may be obtained from the density, the freezing point, and the behaviour of the liquid when it is subjected to slow fractional distillation with a suitable still-head. In connexion with the behaviour on distillation, attention may be directed to the tables recording the observations made by Fox and Barker (*loc. cit.*). The significance of the density and the freezing point will be apparent from table I and the freezing-point relations which have already been described.

In regard to chemical methods, the nitration and bromination processes are of little use when we are dealing with quaternary mixtures. On the other hand, a method described by Skirrow (*J. Ind. Eng. Chem.*, 1917, **9**, 1102), which involves the measurement of the rate of oxidation of the phenols by permanganate in sulphuric acid solution, seems to afford an approximate measure of the percentage of phenol present in quaternary mixtures, although the nature of the admixed cresol has a very appreciable influence on the velocity of the oxidation process.

The information to be derived from the direct application of the freezing-point method to quaternary mixtures is strictly limited, in that only one of the three independent variables, in terms of which the composition of such a mixture may be expressed, can be determined in this way. This variable is the proportion of *p*-cresol, which may be estimated according to the method already described in sections II and III. The applicability of this method to the quaternary mixture depends on the fact that the freezing point of *p*-cresol is lowered to the same extent by equal quantities of phenol, *o*-cresol, and *m*-cresol.

Examples:

(1) $X = 19\cdot5$ per cent. phenol, $20\cdot0$ per cent. *o*-cresol, $36\cdot4$ per cent. *m*-cresol, $24\cdot1$ per cent. *p*-cresol.

$Y = 33\cdot2$ per cent. $X + 66\cdot8$ per cent. *p*-cresol, freezing point $16\cdot15°$, from which per cent. *p*-cresol in $Y = 74\cdot8$, and hence in $X = 24\cdot0$.

(2) $X = 10\cdot0$ per cent. phenol, $20\cdot0$ per cent. *o*-cresol, $56\cdot0$ per cent. *m*-cresol, $14\cdot0$ per cent. *p*-cresol.

$Y = 25\cdot4$ per cent. $X + 74\cdot6$ per cent. *p*-cresol, freezing point $18\cdot9°$, from which per cent. *p*-cresol in $Y = 78\cdot5$, and hence in $X = 15\cdot3$.

Although the direct application of the freezing-point method to quaternary mixtures is thus limited to the estimation of *p*-cresol, it appears to be possible to analyse such mixtures completely by physical methods if the mixtures are subjected to a preliminary fractionation. In carrying out this process, the quaternary mixture X is mixed with about half its weight of *o*-cresol, following the device recommended by Fox and Barker (*loc. cit.*) in connexion with the estimation of phenol. This mixture, X', is then submitted to slow fractional distillation with a still-head of the Raschig type, and by this means X' is separated into two fractions, one of which (A) consists of a mixture of phenol and *o*-cresol and the other (B) of a mixture of *o*-cresol, *m*-cresol, and *p*-cresol. The fractions A and B are then analysed by application of the freezing-point methods, which have been already described in sections I and III.

As yet it has not been possible, in view of the urgency of other work, to test this method in any detail, but the preliminary observations which have been made seem to show that satisfactory results for quaternary mixtures containing phenol and the three cresols may be obtained in this way.

In reference to the application of the freezing-point methods which have been described, it should be explained that great care is needed to ensure that the materials used are free from water. The tables of data and the corresponding curves may only be applied directly to the interpretation of freezing points determined by other observers when the standard samples of phenol and of the cresols have freezing points which are identical with those of the samples used by us. With regard to these samples, it is probable that pure anhydrous phenol melts at about 41°, and our use of phenol melting at 40·5° was determined by the fact that a substance of this melting point could readily be prepared from ordinary samples of phenol. The melting point of *o*-cresol (30·45°)

is slightly higher than that recorded in the literature, but we have found that *o*-cresol of this quality may readily be obtained from the commercial product. The *m*-cresol (m. p. 10·0°) was probably not quite pure, although this temperature is much higher than that previously recorded. With regard to the *p*-cresol, it may be mentioned that a substance of this melting point (34·15°) was obtained from two different samples of synthetic material. This temperature is lower than that recorded by certain observers, but agrees fairly closely with the value of 33·8° given by Sidgwick, Spurrell, and Davies (*loc. cit.*), and by Bramley (*loc. cit.*). The use of standard materials differing but slightly in freezing point from those employed by us does not prevent the use of the tables of figures recorded in the paper, for experience has shown that it is possible to make suitable allowance for such differences if these are small. In actual practice, it will no doubt be found preferable to draw up corresponding tables which are directly applicable to the available standard substances and to such modified conditions of working as may seem advisable. These are matters of detail which do not affect the general methods of procedure which have been described.

Summary.

An account is given of the application of physical methods in the analysis of the technically important series of mixtures: (*a*) phenol and *o*-cresol, (*b*) *m*-cresol and *p*-cresol; (*c*) *o*-cresol, *m*-cresol, and *p*-cresol, (*d*) phenol, *o*-cresol, *m*-cresol, and *p*-cresol. It is shown that freezing-point measurements may be utilised for the complete determination of the composition of the binary and ternary mixtures. In the case of the quaternary mixture, the application of the freezing-point methods is preceded by a fractionation process, in which the quaternary is mixed with a known quantity of *o*-cresol and separated into two fractions containing (1) phenol and *o*-cresol, (2) *o*-cresol, *m*-cresol, and *p*-cresol.

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[*Received, August 27th*, 1918.]

LXXXVI.—*The Oxidation and Ignition of Coal.*

By Richard Vernon Wheeler.

This paper contains an abbreviated account of work that has been carried out intermittently during the past nine years, at the outset for the Mining Association of Great Britain (British Coal Dust Experiments Committee) and during later years at the Home Office Experimental Station.

The earlier work (to which Mr. M. J. Burgess contributed the largest share during 1909—1911) was withheld from publication from the desire eventually to present a complete study of the cause of the spontaneous combustion of coal. The main results were, however, communicated privately to individuals particularly interested in the subject, and the conclusions reached were summarised in evidence before the Departmental Committee on Spontaneous Combustion in Coal Mines in 1913 (Minutes of Evidence, first to seventh days).

At a later date, the Doncaster Coal Owners founded a laboratory, under the direction of Dr. J. S. Haldane, to specialise in the study of the spontaneous combustion of coal, and a series of papers has emanated from that laboratory (*Trans. Inst. Min. Eng.*, 1914, **46**, 563; 1915, **48**, 503; **49**, 35; 1916, **51**, 493; **52**, 338; 1918, **54**, 197). This series of papers renders the publication of the details of much of the work herein summarised unnecessary, for although the experiments were carried out in a different manner they have little to add to the results obtained at Doncaster.

The first method of experiment adopted was to circulate air or oxygen in a closed system through a column of powdered, freshly-won coal, heated in a constant-temperature oven, and to measure the rate of disappearance of oxygen by the rate of diminution of pressure in the system. Samples of the gases were taken at intervals throughout an experiment (some of which were continuous during several weeks) by means of by-passed sampling tubes so arranged that the removal of the sample did not alter the pressure in the circulation system.

It may be said at once that the results obtained by these means did not afford as much information as was desired or expected, and other methods of experiment, shortly to be described, were ultimately adopted. It was found, in conformity with the results of earlier and recent investigators*:

* A review of the more important work on spontaneous combustion is contained in Professor W. A. Bone's recent book, "Coal and its Scientific Uses" (London, 1918), pp. 149—163.

(1) That the absorption of oxygen by newly-won bituminous coal is initially very rapid, even at ordinary atmospheric temperatures, but that this rapid absorption soon gives place to a slow but long-continued absorption.

(2) That the initial rapid absorption of oxygen at low temperatures is not accompanied, so far as could be ascertained, by the formation of water or the oxides of carbon, but that during the second, slow phase of the absorption these products of oxidation of the coal substance make their appearance, the amounts increasing with the temperature of the coal.

(3) That the ratio CO_2/CO in the products of combustion remained appreciably constant for a given coal at a given temperature throughout the period of long-continued slow absorption of oxygen, the ratio decreasing with increased temperature.

These facts did not, however, bring one much nearer to an explanation of the mechanism of the reaction between oxygen and coal that results in "spontaneous combustion," and they gave no indication of the reason why one coal is more liable to self-heat than is another.

The Oxidation of Coal.

It has already been stated that during the rapid absorption of oxygen that takes place when newly-won coal is exposed to air at atmospheric temperature, the simultaneous formation of carbon dioxide or carbon monoxide could not be detected, although both these gases make their appearance subsequently. It had been noticed, however, that the "occluded gases" that can be removed from any sample of coal by exhaustion at 100° contain a high proportion of the oxides of carbon if the coal has been previously "weathered," either naturally or artificially, thus differing from the gases withdrawn from newly-won coal, which consist mainly of methane and the higher members of the paraffin series of hydrocarbons (see Burgess and Wheeler, T., 1914, **105**, 131).

From this it was thought that there might be a reaction between oxygen and some part of the coal substance analogous to that between carbon and oxygen, investigated by Rhead and Wheeler (T., 1913, **103**, 461), which is characterised by the fixation of oxygen, the presumption being that an unstable compound of carbon and oxygen is formed.

Experiments were therefore made with the intention of examining more closely the composition and occurrence of the occluded gases in artificially weathered coal. Freshly-won coal * from that

* The coal as soon as it was hewn was packed tightly in a box which was hermetically sealed and dispatched the same day to the laboratory.

portion of the Thick Coal Seam at Hamstead Colliery, termed "Slips," was roughly crushed and thoroughly exhausted at 100° to free it from naturally occluded gases, 230 grams being taken for the experiment. Undried air was then slowly drawn through the coal at a temperature of 15° during forty-eight hours, and, after the apparatus had been rapidly exhausted by means of a Geryk oil-pump, any gases contained in the coal were extracted by a Sprengel mercury pump and collected. The results were:

	Analysis, per cent.			
	CO_2.	O_2.	CO.	N_2.
Gases removed at 15°	11·18	4·2	nil	84·0
Gases removed between 15° and 100° ...	43·5	20·6	6·9	29·0

A total volume of 31·5 c.c. of gases (measured at 0° and 760 mm.) was removed from the coal.

This experiment gives a definite indication that, whereas some oxygen is occluded by coal at 15° and can be removed therefrom as such by physical means, the major portion of the oxygen retained by the coal only makes its appearance as oxides of carbon when the temperature of the coal is raised.

The same weight (230 grams) of newly-won coal, roughly crushed, from the "Brazils" portion of the Thick Coal Seam, Hamstead Colliery, was treated in a similar manner: the naturally occluded gases having been removed, air was aspirated through the coal during twenty-four hours; most of the air in the apparatus having been removed at the ordinary temperature by several strokes of a Geryk oil-pump, the temperature of the coal was raised to 100° and the gases were collected, no separation being made between the gases removed at 15° and at 100°, as with the "Slips" coal. This series of operations was performed several times with the variations in treatment described in the table on p. 948.

It will be seen that, under similar treatment, the "Brazils" coal yielded less gases than did the same weight of the "Slips" coal. A more important observation is the marked increase in the quantity of gas retained by the coal when the air passed over it was dried by calcium chloride. To confirm this, a series of experiments was made in a slightly different manner, using 100 grams of "Brazils" coal that had been crushed so as to pass through a 10 × 10 and remain on a 30 × 30 mesh sieve, and from which the naturally occluded gases had been removed.

After treatment of the coal with air (either saturated with water vapour at 15° or dried by passing through calcium chloride towers) during six hours at different temperatures, the apparatus

Treatment.	Volume of gases removed up to 100°. c.c. at 0° and 760 mm.	Analysis, per cent. CO_2.	O_2.	CO.	N_2.
A. Undried air aspirated through the coal during 24 hours at 15°	18·9	11·9	5·1	2·3	80·7
B. Air dried by calcium chloride aspirated through the coal during 24 hours at 15°	40·3	15·5	8·7	3·2	72·6
C. As with B	45·0	25·5	3·7	2·3	68·5
D. As with A	24·0	16·8	13·4	1·3	68·5
E. Air saturated with water-vapour at 15° aspirated through the coal during 24 hours at 15°...	22·0	25·8	12·6	3·4	58·2
F. Air saturated with water-vapour at 15° aspirated through the coal during 24 hours at 50°.........................	23·4	49·7	8·8	5·3	36·2
G. Air dried by calcium chloride aspirated through the coal during 24 hours at 50°	32·5	29·7	7·3	5·5	57·5

was thoroughly exhausted at the ordinary temperature by a Sprengel mercury pump, and only those gases collected that were withdrawn from the coal when its temperature was raised from 15° to 100°. The results were:

Treatment.	Volume of gases removed between 15° and 100°. c.c. at 0° and 760 mm.	Analysis. CO_2.	O_2.	CO.	N_2.	Ratio. CO_2/CO.
A. Moist air at 15°.........	17·7	28·0	2·8	2·2	67·0	12·7
B. Dried air at 15°.........	30·8	15·4	nil	1·8	82·8	8·6
C. Moist air at 50°	18·7	42·0	4·7	3·9	49·4	10·8
D. Dried air at 50°	27·0	12·8	1·5	1·7	84·0	7·5
E. Moist air at 100°	6·8	77·0	1·8	13·2	8·0	5·8
F. Dried air at 100°	8·9	31·3	0·2	8·3	60·2	3·8

These results, apart from the difference observable between the effects of moist and dried air (a matter requiring further study), bear a striking resemblance to the result of passing air over carbon at low temperatures, and a similar explanation of them can be offered, namely, that "the first step in the oxidation of coal is the formation of an addition compound, or complex, of oxygen with one or more of the substances present in coal."

This conclusion, founded on the results of experiments of a different character from those described in this paper, has been put

forward also by Porter and Ralston ("A Study of the Oxidation of Coal," United States Bureau of Mines, Technical Paper 65, 1914), from whose paper the foregoing quotation is made. Porter and Ralston continue: "This complex is unstable and decomposes readily—more readily with some coals than with others—setting free water, CO_2, and CO."

It should not be supposed that the similarity in the behaviour of oxygen towards both coal and carbon is indicative of the presence of "free" carbon in coal. Experimental evidence as to the existence of free carbon as a normal constituent of coal is difficult, if not impossible, to obtain. This matter has been discussed by Jones and Wheeler (T., 1916, **109**, 709), who have pointed out that none of the factors, singly or combined, involved in the formation of coal can have brought about the complete carbonisation of any portion of the substances from which it is formed. On the other hand, the existence in coal of substances the molecules of which are similar in type to the carbon molecule must be presumed. Dimroth and Kerkovius (*Annalen*, 1912, **399**, 120) have shown that the carbon molecule contains the fluorene grouping, whilst Pictet and Ramseyer (*Ber.*, 1911, **44**, 2486) have extracted hexahydrofluorene from Montrambert coal. Moreover, both carbon and coal yield benzenehexacarboxylic acid (mellitic acid) on oxidation, showing that in both there are molecules present the structure of which involves a six-carbon ring, each carbon atom of which is attached to an additional carbon atom.

In order to discover the exact nature of the compounds thus presumed responsible for the "first step in the oxidation of coal," a more intimate knowledge is required than is possessed at present of the chemical constitution of the coal substance. A solution of the problem of the spontaneous combustion of coal is, in fact, largely dependent on the success of the endeavours that are being made to resolve the coal conglomerate into its component parts. No doubt suitable "oxidation" experiments will contribute towards this end, inasmuch as they should afford information regarding the chemical characteristics of different parts of the coal conglomerate.

The Ignition of Coal.

The reaction between oxygen and coal that results in the "fixation" of the oxygen is accompanied by a heating effect, so that if pains are taken to prevent the dissipation of heat, the temperature of the coal rises. An increase in the temperature of the coal increases its rate of reaction with oxygen; if the rate of reaction is productive of more heat per unit of time than is sufficient to

counterbalance loss incidental to the physical conditions obtaining, it follows that eventually the coal will ignite.

Thus it is that spontaneous fires may occur in coal, in the mine or on the surface; and thus it is that several factors other than the chemical constitution of the coal have to be considered when attempting to guard against such fires. On the chemical constitution of the coal the rate of its reaction with oxygen at a given temperature mainly depends, but its state of division, permeability, and physical condition generally, also affect the rate of reaction; whilst the rate of dissipation of heat is governed by such factors as the amount of ventilation and the thermal conductivity of the coal itself and of its surroundings.

When determining the relative ignition-temperatures of different coals, it is not easy to decide what criterion of "ignition" should be employed. If one adopts the generally accepted definition of "ignition-temperature" as applied to gaseous mixtures (that is, that temperature at which self-heating of the mixture begins to take place), the ignition-temperature of most coals is the normal atmospheric temperature. A distinction between one coal and another could no doubt be made by determining the time taken for this self-heating from atmospheric temperature to result in flame under standard conditions.

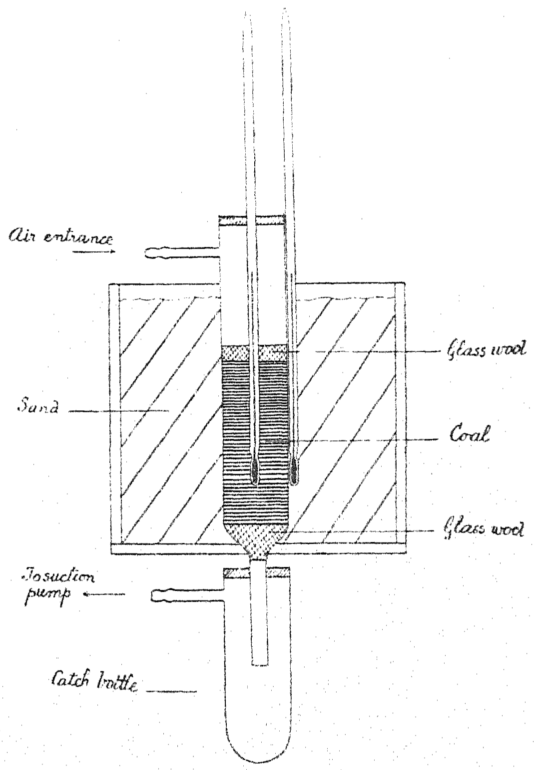
It may be of value also to know at what temperature a given coal must be heated in air, under specified conditions, in order that it shall burst into flame, and this temperature may perhaps be regarded as the "ignition-temperature," the preliminary self-heating (corresponding with the "pre-flame period" with gases) being ignored. Experimental difficulties, however, stand in the way both of determining accurately the moment when flame first appears in a mass of coal, and of ensuring that in comparative tests with different coals all the factors on which the appearance of actual flame depends are maintained constant.

From a practical as well as from a theoretical point of view, it is sufficient to know at what temperatures, under standard conditions, different coals begin to react with oxygen so rapidly that the ultimate appearance of flame is assured. If, for example, air is drawn at a constant speed through a column of powdered coal, the temperature of which is gradually raised by an external source of heat, eventually the temperature within the coal will begin to rise rapidly above that of the external source of heat. It is then only a matter of time, depending on the physical conditions of the test, before the coal will inflame.

In order to determine what relationship, if any, there is between the chemical composition of a coal and its ignition-temperature, a

number of coals were tested in the following manner. Forty grams of the powdered coal that had passed through a 150 × 150 and remained on a 240 × 240 mesh sieve were placed in a glass tube of the form shown diagrammatically in Fig. 1, making a column about 12 cm. long. This tube was fixed vertically in an electrically heated sand-bath, and a current of air (dried by passing through calcium chloride towers) drawn through it at a constant

FIG. 1.



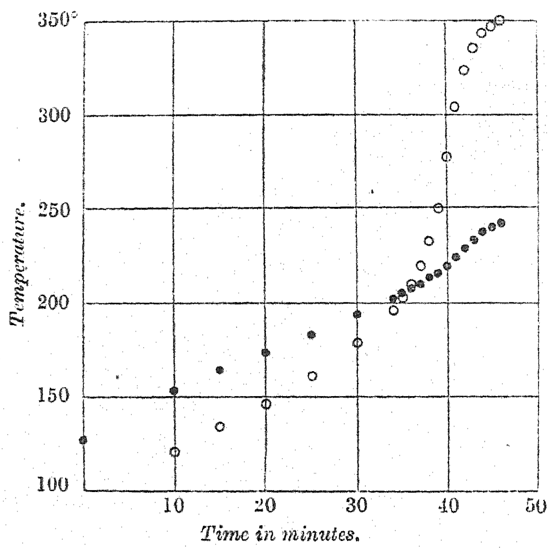
speed. The temperature of the sand-bath was then slowly raised, at a uniform rate, and simultaneous readings of two thermometers, the one embedded in the coal and the other in the sand, taken at frequent intervals of time.

In this manner, two time–temperature curves were obtained, the one showing the rate of rise of temperature of the sand-bath and the other the rate of rise of temperature of the coal. At a given temperature, depending on the coal employed, these two curves cut

one another. This temperature was taken to be the ignition-temperature of the coal relative to other coals tested in the same manner.

In Fig. 2, an example of the results obtained is given. Only the later portions of the two curves are shown; during the earlier stages of the heating (from atmospheric temperature) the curves run parallel to each other. It will be seen that the temperature at which the reaction-velocity became so rapid that the inflammation of the coal was imminent is clearly indicated at about 205°. It is evident also from the gradual approach of the two curves that the heat due to oxidation of the coal was sufficient, despite loss to

FIG. 2.



the outgoing air, to raise the temperature of the coal above that normally due to the heat received from the sand-bath when the reaction was proceeding at a temperature of 125°. The latter temperature might be regarded as the ignition-temperature of the coal (that is, the temperature at which self-heating began) under the conditions of the experiment. For comparative purposes, however, it was found preferable to record, as the relative ignition-temperature, the point at which the coal temperature curve and the sand-bath temperature curve cut one another, for this point is clearly defined. It is the temperature at which rapid self-heating begins, and is therefore in conformity with Nernst's definition of the ignition-temperature for gaseous mixtures.

In the table that follows are given the relative ignition-temperatures as thus determined for a number of bituminous coals. Full analyses of the coals, which are referred to under laboratory numbers, have been published in the Second Report of the Explosions in Mines Committee (H.M. Stationery Office, Cd. 6431 of Session 1912—1913).* The oxygen-contents only are reproduced here, for if reference be made to the full analyses it will be seen that no relationship exists between the ignition-temperatures now recorded and other analytical data.

Coal number.	Oxygen-content. (Per cent. on ash-free dry coal.)	Relative ignition temperature.	Coal number.	Oxygen-content. (Per cent. on ash-free dry coal.)	Relative ignition temperature.
213	11·1	165°	247	8·3	182°
210	11·1	165	240	8·1	180
218	11·1	167	216	8·0	183
248	10·6	177	224	7·6	192
251	10·5	176	226	7·4	188
234	10·3	176	200	7·3	185
207	9·9	177	205	7·0	192
246	9·9	179	239	6·7	195
208	9·9	179	215	6·6	206
211	9·5	178	230	6·4	200
235	9·2	178	214	5·6	210
231	8·8	183	203	5·4	200
201	8·8	187	217	5·1	217
206	8·7	186	232	4·9	195
241	8·6	183	227	4·7	220
225	8·5	185	228	3·9	200

It is clear from this table that the statement made by several investigators, that the most highly oxygenated fuels are those most liable to self-heat, a statement intended to distinguish between the different classes of fuels—lignitic, bituminous, and anthracitic—holds with remarkable closeness for coals of the same class (bituminous).

If it is correct to assume that the similarity in behaviour towards oxygen evinced by bituminous coal and carbon is due to the presence in the coal of groups of compounds the molecules of which have aromatic structures resembling those of the carbon molecule, it follows that the greater the proportion of such groups of compounds in a coal the greater will be the ability of that coal when newly-won to "attach" oxygen, and the higher will be its proportion of oxygen when "saturated."

The oxygen-contents given in the table must be regarded as those of the "saturated" coals; for the treatment to which the coals had been subjected—their pulverisation and sieving—involved the exposure of the fine dusts to air at 15° for a length of time sufficient

* A certain number of the analyses are recorded also in T., 1913, 103, 1722.

to saturate them with oxygen at that temperature. Since the samples taken for the combustion analyses were accorded the same treatment as the samples tested for ignition-temperatures, the relationship between oxygen-content and ignition-temperature is not affected by this saturation with oxygen; but it is necessary to remember that some of the oxygen recorded as present in each coal must be in the form of the presumed complex.

It is not remarkable that a coal containing a high proportion of oxygenated compounds should show signs of rapid self-heating in an air-stream at a temperature lower than that required by a coal of less oxygen-content. What is known of the constitution of coal points to the major portion of the oxygenated compounds normally present being compounds arising from the degradation of the celluloses and compound celluloses of the cell-walls of the coal-plants. It is just these compounds of which the structures of the molecules approximate most closely in character to those of carbon, which therefore may presumably act like carbon in causing a loose attachment of oxygen. A coal rich in such compounds—oxygenated compounds—might therefore be expected to absorb oxygen readily and, *ipso facto*, to self-heat readily.

The term "self-heat" may, moreover, be seen to have its true significance so far as a highly oxygenated, "saturated," coal is concerned if one considers that the loosely combined oxygen may at a higher temperature desire a more permanent attachment—may, so to say, bite where previously it has only nibbled. If any reaction of this nature does indeed take place, an evolution of heat should be observed when a "saturated" coal is heated slowly in a vacuum or in an inert atmosphere. Hollings and Cobb (*J. Gas Lighting*, 1914, **126**, 917), in the course of their study of the thermal phenomena occurring during carbonisation, obtained several heating curves which show a marked exothermic reaction (in an atmosphere of nitrogen) between 150° and 250°. Hollings and Cobb at a later date (T., 1915, **107**, 1109) stated that they attached no importance to deflexions of their heating curves at temperatures lower than 200°, apparently because they considered it "hardly possible that between 150° C. and 250° C. there can be any exothermic reaction in an inert atmosphere" (*loc. cit.*, p. 920); but the deflexions shown in their earlier paper are too large to be ignored. It is significant that the range, 150° to 250°, over which the exothermic reaction with coal in a stream of nitrogen is manifest in Hollings and Cobb's experiments should correspond so closely with the range over which, with the series of coals tested in the present research, rapid self-heating occurs in a stream of air.

The lines upon which the researches are being continued are obvious. At their present stage, the following working hypothesis can be advanced: The reaction responsible for the "self-heating" of coal is mainly one of attachment of oxygen to molecules of high carbon-content. Subsidiary to this reaction, but playing an important part in determining the actual spontaneous ignition of coal, is a chemical interaction between the oxygen thus loosely held, by the carbon-like molecules, and other atoms in those molecules, or other portions of the coal conglomerate.

I wish to acknowledge the assistance of Mr. C. B. Platt during the experiments described under the heading "The Oxidation of Coal," and of Messrs. M. J. Burgess and T. F. E. Rhead during the experiments on the ignition of coal.

[*Received, October* 12*th*, 1918.]

LXXXVII.—*Studies in the Tetrahydronaphthalene Series.*

By ARTHUR G. GREEN and FREDERICK MAURICE ROWE.

A. ar-*Tetrahydro-α-naphthylamine.*

ar-TETRAHYDRO-α-NAPHTHYLAMINE has been shown to possess many interesting peculiarities. It has the general properties of an aromatic amine, yet, whilst on the one hand it resembles aniline and its homologues (particularly *o*-2-xylidine) rather than α-naphthylamine (Bamberger, *Annalen*, 1890, **257**, 11), on the other it is similar to α-naphthylamine in the facility with which it reacts with diazonium salts, forming aminoazo-derivatives far more readily than does *o*-2-xylidine (Noelting and Forel, *Ber.*, 1885, **18**, 2682). Of further interest is the fact that azo-dyes derived from *ar*-tetrahydro-α-naphthylamine differ considerably in shade from similar azo-dyes derived from α-naphthylamine, and in this respect approximate to dyes derived from benzenoid amines (Bamberger, *Ber.*, 1887, **20**, 2915; Bamberger and Bordt, *ibid.*, 1889, **22**, 625; Morgan and Richards, *J. Soc. Chem. Ind.*, 1905, **24**, 652). In view of the possible importance of tetrahydro-α-naphthylamine in the technology of dyes, it appeared desirable to investigate more closely the formation of this base and also to attempt to prepare a number of its previously unknown deriv-

atives in order to compare their properties with those of benzenoid and naphthalenoid compounds of corresponding type.

ar-Tetrahydro-α-naphthylamine was obtained by Bamberger and Althausse (*Ber.*, 1888, **21**, 1786) by reducing α-naphthylamine with sodium and boiling amyl alcohol. This reaction appears to be a general one for the preparation of hydrogenated naphthalene derivatives, a considerable number of which were prepared by Bamberger and his numerous collaborators (*loc. cit.*). It is usually carried out by reducing a boiling solution of the substance in ten times its weight of amyl alcohol with one and a-half to twice the theoretical quantity of sodium (Bamberger and Lodter, *Ber.*, 1877, **20**, 3073). The yield and character of the product vary with the individual substance reduced, α-derivatives of naphthalene giving rise to aromatic, whereas β-derivatives form mainly alicyclic compounds. Thus it was found (Bamberger and Müller, *Ber.*, 1888, **21**, 850; Bamberger and Kitschelt, *Ber.*, 1890, **23**, 876) that the main product obtained by reducing β-naphthylamine was *ac*-tetrahydro-β-naphthylamine, together with a small quantity of *ar*-tetrahydro-β-naphthylamine. On the other hand, *ar*-tetrahydro-α-naphthylamine is stated to be the sole product when α-naphthylamine is reduced, the isomeric alicyclic compound having only been obtained from *ac*-tetrahydro-5-amino-1-naphthylhydrazine (Bamberger and Bammann, *Ber.*, 1889, **22**, 964).

The influence of the particular alcohol used as solvent on the yield of product was also investigated by Bamberger, who found that in the reduction of β-naphthylamine, replacement of amyl alcohol by ethyl alcohol results in a minimum yield of the tetrahydro-derivative, and concluded that the course taken by the reaction and the yield obtained were intimately connected with the boiling point of the solvent employed. Later experiments (Bamberger and Müller, *Ber.*, 1888, **21**, 1112), using such solvents as hexadecyl alcohol, phenol, glycerol, and mixtures of amyl alcohol and vaselin, did not, however, support this hypothesis, at least in the case of β-naphthylamine.

We have now studied the conditions governing the conversion of α-naphthylamine into *ar*-tetrahydro-α-naphthylamine. When amyl alcohol was used as the solvent and the reduction carried out as described by other workers, a yield of 70 per cent. of the theoretical was obtained. It was found that when amyl alcohol was replaced by ethyl alcohol, the α-naphthylamine remained unaltered and no *ar*-tetrahydro-α-naphthylamine could be detected. Similarly, α-naphthylamine was not changed by treatment with sodium when butyl alcohol was used as solvent, and the addition of butyl alcohol to amyl alcohol produced a diminution in yield

proportional to the quantity of butyl alcohol in the mixture. Moreover, in an experiment in which butyl alcohol was employed under pressure sufficient to raise the boiling point to that of amyl alcohol under normal pressure, no trace of *ar*-tetrahydro-α-naphthylamine could be detected. The difference in the behaviour of amyl alcohol from other alcohols cannot therefore be due to differences in boiling point, and as the reaction is always accompanied by the destruction of from 10 to 15 per cent. of the amyl alcohol used, it is probable that the reduction is intimately connected with the oxidation of amyl alcohol, and not simply due to direct hydrogenation.

The effect of the presence of (1) sodium amalgam, (2) mercurous chloride, (3) a nickel catalyst, (4) dextrose, on the reaction with sodium in butyl-alcoholic solution was also studied, but in no case could the tetrahydro-base be detected.

Sabatier and Senderens succeeded in preparing tetrahydronaphthalene by reducing naphthalene with hydrogen in the presence of nickel (*Compt. rend.*, 1901, **132**, 1254). We have now tried to prepare *ar*-tetrahydro-α-naphthylamine by the nitration and reduction of tetrahydronaphthalene. Although nitrations were carried out under a variety of conditions, in all cases oxidation took place and no nitro-derivative was isolated.

The *ar*-tetrahydro-α-naphthylamine required for our subsequent experiments was prepared by reducing a boiling amyl-alcoholic solution of α-naphthylamine with sodium The mixture was poured into water, the amyl alcohol layer separated, acidified with hydrochloric acid, and the amyl alcohol removed by distillation in a current of steam. The residue was filtered from a little tar and allowed to crystallise, when the hydrochloride of *ar*-tetrahydro-α-naphthylamine separated in large, colourless tables similar in appearance to aniline hydrochloride. The mother liquors from a number of preparations were united and concentrated, whereby a further quantity of the hydrochloride was obtained. The filtrate from this was basified, and the separated base examined. It was found that whereas pure *ar*-tetrahydro-α-naphthylamine condenses with 4-chloro-1:3-dinitrobenzene to form 2:4-dinitrophenyltetrahydro-α-naphthylamine, a compound crystallising in orange-red plates or needles melting at 134°, the base from the mother liquors when similarly treated gave, together with this compound, an isomeric substance crystallising in golden-yellow leaflets melting at 121°. The two compounds could be readily separated in a pure condition, as the former is less readily soluble in alcohol than the latter. This observation pointed to the presence in the mother liquors of *ac*-tetrahydro-α-naphthylamine. This was isolated by

passing carbon dioxide through a solution of the mixed bases in light petroleum, when the crude carbonate of the alicyclic compound separated. The base after purification proved to be identical with *ac*-tetrahydro-α-naphthylamine described by Bamberger and Bammann (*loc. cit.*).

α-Naphthylamine on reduction, therefore, gives mainly the *ar*-tetrahydro-base, together with a small quantity of the *ac*-tetrahydro-base, whereas in the case of β-naphthylamine the proportion of alicyclic and aromatic tetrahydro-bases is reversed.

B. *Nitro-derivatives of* ar-*Tetrahydro-α-naphthylamine.*

Morgan, Micklethwait, and Winfield (T., 1904, **85**, 737) state that the changes involved on nitrating *ar*-tetrahydro-α-naphthylamine and its acyl derivatives are somewhat complex. We have now examined the process more closely, and have prepared and examined the mono- and di-nitro-derivatives of *ar*-tetrahydroaceto-α-naphthalide and the corresponding nitroamines.

When *ar*-tetrahydroaceto-α-naphthalide is nitrated in cold sulphuric acid solution with one molecular proportion of nitric acid, a nitro-derivative is formed, together with a considerable proportion of an uncrystallisable resin. The formation of resins in this and other cases may possibly be due to the presence of a small quantity of the alicyclic isomeride in the material employed. The product proved to be a mononitro-compound. It is readily reduced to the monoacetyldiamine melting at 156°, which on treatment with acetic anhydride is converted into the diacetyldiamine, melting at 291°, described by Morgan, Micklethwait, and Winfield (*loc. cit.*). The nitro-group is therefore in the para-position with respect to the acylamino-group. In no case was the presence of the isomeric ortho-nitro-derivative detected.

The para-nitroamine itself is readily obtained by the hydrolysis of the acetyl derivative with alkalis or acids, and is similar in appearance and properties to *p*-nitroaniline. It is converted on reduction into *ar*-tetrahydro-1:4-naphthylenediamine.

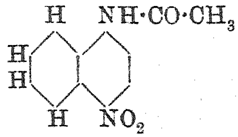
4-Nitro-*ar*-tetrahydro-α-naphthylamine may be diazotised and coupled, forming azo-dyes, the shades of which approximate more nearly to those of azo-dyes of similar type derived from benzenoid than from naphthalenoid bases.

When the quantity of nitric acid was increased to two molecular proportions and the nitration carried out as before, another product was obtained which, after separation from resinous impurities by crystallisation from alcohol, proved to be a dinitro-compound. This substance is also formed by the further nitration of 4-nitro-

ar-tetrahydroaceto-α-naphthalide. The dinitrotetrahydro-α-naphthylamine itself is readily obtained by warming the acetyl derivative with sulphuric acid.

Both the mono- and di-nitroamines form quinonoid salts with alkalis (compare T., 1913, **103**, 508). The mononitro-compound gives an orange-red potassium salt and the dinitro-compound a bluish-green potassium salt. In the former case, the salt dissociates rather more readily than we found to be the case with other quinonoid salts of nitroamines.

4-Nitro-ar-*tetrahydroaceto-α-naphthalide*,

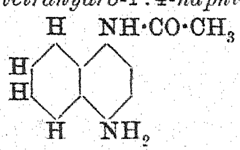


Ten grams of tetrahydroaceto-α-naphthalide, melting at 154°, prepared as described by Morgan, Micklethwait, and Winfield (*loc. cit*), were dissolved in 16 c.c. of 100 per cent. sulphuric acid. The solution was cooled to −10° in a freezing mixture and nitrated at that temperature by the addition of a mixture of 3·6 c.c. of nitric acid (one molecular proportion, D 1·4) and 9 c.c. of 100 per cent. sulphuric acid. On recrystallisation of the product from dilute alcohol or boiling water, *4-nitro*-ar-*tetrahydroaceto-α-naphthalide* was obtained in colourless, slender needles melting at 178°. It is readily soluble in organic solvents, but less readily so in water:

0·1864 gave 19·3 c.c. N_2 at 19° and 756 mm. N = 11·88.
$C_{12}H_{14}O_3N_2$ requires N = 11·96 per cent.

0·01248 required 10·1 c.c. $TiCl_3$ (1 c.c. = 0·001772 gram Fe). Calculated as $C_{10}H_{10}(NH{\cdot}CO{\cdot}CH_3){\cdot}NO_2$ = 99·85 per cent., that is, 6H required for reduction.

1-Acetyl-ar-*tetrahydro-1:4-naphthylenediamine*,



Five grams of iron powder, 1 gram of acetic acid (30 per cent.), and 15 c.c. of water were placed in a flask, and 6·5 grams of finely powdered 4-nitro-*ar*-tetrahydroaceto-α-naphthalide were added in small portions at a time. The flask was well shaken, and the

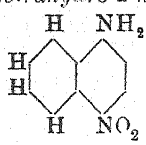
temperature rose as the reduction proceeded. When the contents of the flask had lost their yellow colour, the mixture was filtered hot and the residue boiled several times with water and filtered. The united filtrates were extracted with ether, and colourless, rhombic plates or needles of 1-*acetyl*-ar-*tetrahydro*-1:4-*naphthylenediamine*, melting at 156°, separated from the ethereal solution:

0·1452 gave 17·2 c.c. N_2 at 20° and 762 mm. N = 13·62.
$C_{12}H_{16}ON_2$ requires N = 13·72 per cent.

1·20 required 5·85 c.c. *N*-$NaNO_2$. Calculated as $C_{10}H_{10}(NH{\cdot}CO{\cdot}CH_3){\cdot}NH_2$ = 99·6 per cent.

It is readily soluble in water, dilute acids, or organic solvents. By treatment with acetic anhydride, it is converted into the diacetyldiamine, which forms colourless needles melting at 291°. It may be diazotised and combined with amines and phenols. For example, with 2-naphthol-3:6-disulphonic acid, a dye is formed which gives a reddish-brown shade on wool similar to that obtained with the corresponding compound derived from acetyl-*p*-phenylenediamine (Azo Corallin L).

4-Nitro-ar-*tetrahydro-α-naphthylamine*,



4-Nitrotetrahydroaceto-α-naphthalide is hydrolysed readily on boiling the alcoholic solution for ten minutes with sodium hydroxide. The nitroamine crystallises from the yellow solution on cooling, and on recrystallisation from dilute alcohol was obtained in pale yellow needles, melting at 116°. It is readily soluble in organic solvents or dilute acids, but less readily so in water. Hydrolysis may be effected equally well by boiling with dilute sulphuric acid or hydrochloric acid:

0·1236 gave 15·5 c.c. N_2 at 18° and 756 mm. N = 14·45.
$C_{10}H_{12}O_2N_2$ requires N = 14·58 per cent.

2·25 required 11·7 c.c. *N*-$NaNO_2$. Calculated as $C_{10}H_{12}(NO_2){\cdot}NH_2$ = 99·84 per cent.

0·01 required 9·9 c.c. $TiCl_3$ (1 c.c. = 0·001772 gram Fe). Calculated as $C_{10}H_{10}(NH_2){\cdot}NO_2$ = 100·18 per cent., that is, 6H required for reduction.

On adding hydrochloric acid to an alcoholic solution of 4-nitro-*ar*-tetrahydro-α-naphthylamine, the *hydrochloride* separates in colourless, crystalline needles, which are decomposed by water.

Potassium Salt of 4-Nitro-ar-*tetrahydro-α-naphthylamine*, $NH{:}C_{10}H_{10}{:}NO_2K$.

Nine c.c. of a solution containing 1 gram of potassium hydroxide in 30 c.c. of absolute alcohol were added to a solution of 1 gram of the nitroamine in 100 c.c. of dry benzene. The colour became orange-yellow, but no precipitate separated. When the alcohol was evaporated, however, an orange-red precipitate of the salt was produced, which was washed with dry benzene and ether. The salt is immediately hydrolysed by water, giving the parent nitroamine and potassium hydroxide in solution.

Titration with sulphuric acid gave K = 16·76 (mean).

$C_{10}H_{11}O_2N_2K$ requires K = 16·95 per cent.

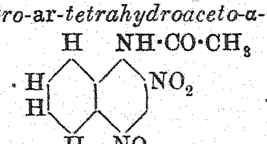
Cotton material padded with alkaline β-naphthol, dried, and passed through a bath of diazotised 4-nitro-*ar*-tetrahydro-α-naphthylamine, is coloured a bright orange-red as compared with the scarlet-red colour of "Para-red."

Diazotised 4-nitro-*ar*-tetrahydro-α-naphthylamine combines with salicylic acid, forming a yellowish-brown precipitate. This *dye* gives an orange-brown shade on chrome-mordanted wool as compared with the reddish-yellow shade which is obtained when chromed wool is dyed with *p*-nitrobenzeneazosalicylic acid (Alizarine Orange R).

4-Nitro-*ar*-tetrahydro-α-naphthylamine is readily reduced to the corresponding diamine by boiling stannous chloride. The colourless, crystalline product which separated was filtered off, dissolved in water, rendered alkaline with sodium hydroxide, and extracted with ether. Excess of acetic anhydride was added to the ethereal solution, and the precipitated diacetyl derivative crystallised from acetic acid. It formed colourless needles melting at 291°.

By oxidising a solution of the hydrochloride of the diamine with chromic acid, followed by extraction with ether, tetrahydro-α-naphthaquinone was obtained. After several crystallisations from light petroleum, it formed pale yellow needles melting at 55°, the temperature given by Bamberger and Lengfeld (*Ber.*, 1890, **23**, 1132).

2:4-*Dinitro*-ar-*tetrahydroaceto-α-naphthalide*,



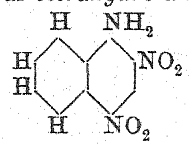
Ten grams of *ar*-tetrahydroaceto-α-naphthalide were dissolved in 16 c.c. of 100 per cent. sulphuric acid. The solution was cooled

to -10° in a freezing mixture, and nitrated at that temperature by the addition of a mixture of 7·2 c.c. of nitric acid (two molecular proportions, D 1·4) and 24 c.c. of 100 per cent. sulphuric acid. The mixture was allowed to remain overnight at the ordinary temperature, and then poured on ice. The crude product was separated and crystallised twice from alcohol, when it formed colourless needles melting at 202°. The same substance is obtained by the further nitration of 4-nitro-*ar*-tetrahydroaceto-α-naphthalide:

0·1148 gave 16·3 c.c. N_2 at 18° and 754 mm. N = 16·36.
$C_{12}H_{13}O_5N_3$ requires N = 16·47 per cent.

0·00943 required 12·8 c.c. $TiCl_3$ (1 c.c. = 0·001772 gram Fe). Calculated as $C_{10}H_9(NH\cdot CO\cdot CH_3)(NO_2)_2$ = 99·8 per cent., that is, 12H required for reduction.

2:4-*Dinitro*-ar-*tetrahydro-α-naphthylamine*,



Dinitro-*ar*-tetrahydroaceto-α-naphthalide was conveniently hydrolysed by triturating to a paste with a little water and dissolving in concentrated sulphuric acid. The solution was warmed to 50° and poured into water. The yellow flocks which separated were collected and crystallised from alcohol. 2:4-*Dinitro*-ar-*tetrahydro-α-naphthylamine* forms small, yellow needles melting at 181°. It dissolves in dilute alkali hydroxide with a crimson colour:

0·1098 gave 16·7 c.c. N_2 at 19° and 765 mm. N = 17·65.
$C_{10}H_{11}O_4N_3$ requires N = 17·72 per cent.

0·01 required 19·5 c.c. $TiCl_3$ (1 c.c. = 0·001446 gram Fe). Calculated as $C_{10}H_9(NH_2)(NO_2)_2$ = 99·85 per cent., that is, 12H required for reduction.

Potassium Salt of Dinitro-ar-*tetrahydro-α-naphthylamine*.

Fifteen c.c. of alcoholic potassium hydroxide, obtained by dissolving 1 gram of potassium hydroxide in 30 c.c. of absloute alcohol, were added to 2 grams of dinitro-*ar*-tetrahydro-α-naphthylamine dissolved in 200 c.c. of dry benzene. A dark bluish-green precipitate of the salt separated, which was collected and washed with dry benzene and ether. The dry salt forms a bluish-

green powder which deflagrates on heating. It is soluble in excess of alcoholic potassium hydroxide with a crimson colour.

Titration with sulphuric acid gave K=13·97 (mean).

$C_{10}H_{10}O_3N_3K$ requires K=14·18 per cent.

C. *Nitro-derivatives of* ar-*Tetrahydro-α-naphthol.*

ar-Tetrahydro-α-naphthol, originally prepared by Bamberger and Althausse (*Ber.*, 1888, **21**, 1892) by diazotising *ar*-tetrahydro-α-naphthylamine and boiling the diazonium compound with sulphuric acid, was shown by Bamberger and Lengfeld (*Ber.*, 1890, **23**, 1127) to possess the properties of a phenol rather than of a naphthol. In preliminary experiments on the nitration of *ar*-tetrahydro-α-naphthol, we have found that direct nitration does not yield satisfactory results, the products being charred and tarry owing to oxidation. It appeared desirable, therefore, first to prepare a sulphonic acid of *ar*-tetrahydro-α-naphthol, and to use this compound for the nitration experiments.

When *ar*-tetrahydro-α-naphthol was treated with sulphuric acid at 100—110°, as in the sulphonation of phenol, it was largely destroyed and no sulphonic acid could be isolated. The same result was obtained when the temperature of sulphonation was reduced to 60—70°. Indirect methods of obtaining the sulphonic acid also failed. Thus, although sodium naphthionate is readily converted into 1-naphthol-4-sulphonic acid by treatment with sodium hydrogen sulphite, followed by boiling with alkali, its tetrahydro-derivative (sodium *ar*-tetrahydro-α-naphthylamine-4-sulphonate) does not react with sodium hydrogen sulphite, a fact dependent on its benzenoid character.

Further, diazotetrahydronaphthalene-4-sulphonic acid when boiled with dilute sulphuric acid gave, as sole product, *ar*-tetrahydro-α-naphthol, the sulphonic group being eliminated by hydrolysis during the reaction.

The *ar*-tetrahydro-α-naphtholmonosulphonic acid was eventually obtained by dissolving *ar*-tetrahydro-α-naphthol in twice its weight of cold concentrated sulphuric acid and allowing the solution to remain for two days. The product was very readily soluble in water, but its sodium salt could be isolated from the sulphonation mixture in the usual manner. On boiling the sulphonic acid with dilute acids, *ar*-tetrahydro-α-naphthol is regenerated.

From analogy to the monosulphonic acid of *ar*-tetrahydro-α-naphthylamine, which was shown by Morgan, Micklethwait, and Winfield (T., 1904, **85**, 742) to contain the sulphonic group in the para-position with respect to the amino-group, it was to be ex-

pected that the monosulphonic acid of *ar*-tetrahydro-α-naphthol would also be the para-compound. That this is the case is obvious from its behaviour on nitration and the properties of the nitro-derivatives.

The above authors, from a study of the reaction of diazonium compounds with 4-bromotetrahydro-α-naphthylamine and with *ar*-tetrahydro-α-naphthylamine-4-sulphonic acid, conclude that the reactivity of the hydrogen atom in the ortho-position with respect to the amino-group, which is such a characteristic feature of the naphthalene molecule, is destroyed when the non-substituted ring undergoes hydrogenation.

In the case of *ar*-tetrahydro-α-naphthol and its para-sulphonic acid, the behaviour towards diazonium compounds is rather different. *ar*-Tetrahydro-α-naphthol combines readily with diazonium compounds, forming azo-dyes. Yet this fact cannot be employed for estimating *ar*-tetrahydro-α-naphthol, as the figures obtained by titrating with $N/10$-*p*-nitrobenzenediazonium chloride solution are too high to agree with a simple para-azo-coupling and too low to agree with a complete formation of the bisazo-dye. This is in agreement with the observation made by Jacobson and Turnbull (*Ber.*, 1898, **31**, 898) that benzenediazonium chloride combines with *ar*-tetrahydro-α-naphthol, forming both the para-monoazo- and the bisazo-dye simultaneously. On the other hand, *ar*-tetrahydro-α-naphthol-4-sulphonic acid in alkaline solution does not combine with diazonium compounds to form azo-dyes. If, however, a diazonium compound is added to an acidified solution of *ar*-tetrahydro-α-naphthol-*p*-sulphonic acid and the mixture is rendered alkaline and then acidified, combination does takes place, the sulphonic group being displaced by the azo-group.

For the nitration experiments, it was found unnecessary to isolate the *ar*-tetrahydro-α-naphthol-4-sulphonic acid. The sulphonation mixture was diluted with water and nitrated with dilute nitric acid in the cold. Whereas all attempts at direct nitration of *ar*-tetrahydro-α-naphthol had proved unsatisfactory, approximately theoretical yields were obtained by nitrating the sulphonic acid under these conditions.

When one molecular proportion of nitric acid was used for nitration, the mixture set to a mass of yellow, needle-shaped crystals readily soluble in water, which proved to be a mononitro-*ar*-tetrahydro-α-naphtholsulphonic acid.

The sulphonic group of the nitrosulphonic acid was readily hydrolysed by boiling with dilute sulphuric acid. The product, mononitro-*ar*-tetrahydro-α-naphthol, is readily volatile with steam, forms orange-coloured salts with alkalis, and condenses with diazonium

compounds, forming azo-dyes. This behaviour is very similar to that of *o*-nitrophenol, and the compound is presumably an ortho-derivative.

By increasing the quantity of nitric acid to two and a-half molecular proportions and nitrating in the same manner, the nitro-sulphonic acid separated as before, but on warming the mixture to 50°, the product became insoluble in cold water. This compound proved to be dinitro-*ar*-tetrahydro-α-naphthol.

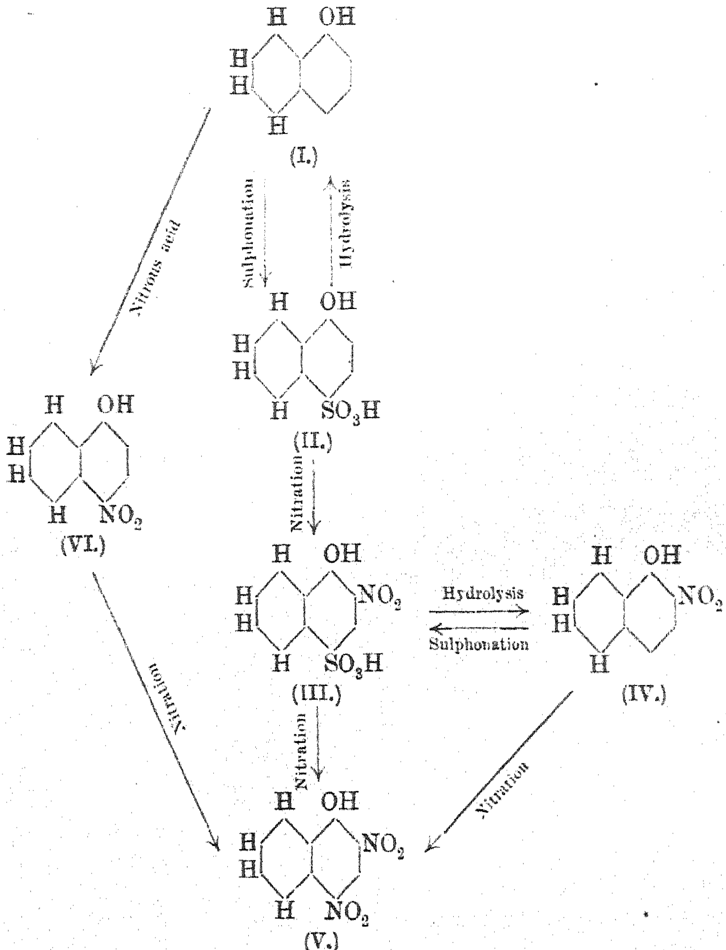
In order to obtain 4-nitro-*ar*-tetrahydro-α-naphthol, an attempt was made to prepare the corresponding nitroso-derivative. By the action of one molecular proportion of nitrous acid on *ar*-tetrahydro-α-naphthol, there was obtained, together with unaltered tetrahydro-α-naphthol, a product which crystallised in yellow needles melting at 163°. This substance did not give Liebermann's nitroso-reaction and was not affected by alkaline potassium ferricyanide. Analysis proved it to be a mononitro-*ar*-tetrahydro-α-naphthol. By increasing the amount of nitrous acid to two molecular proportions, the whole of the *ar*-tetrahydro-α-naphthol was converted into this nitro-compound. It was not volatile with steam, formed yellowish-brown salts with alkalis, and did not condense with diazonium compounds. The properties of the compound are similar to those of *p*-nitrophenol, and the substance is presumably the paranitro-derivative of tetrahydro-α-naphthol.

On further nitration, both mononitro-derivatives give rise to the above dinitro-compound. The relationship of these compounds is therefore shown by the scheme on p. 966.

On account of the importance of 2:4-dinitrophenol in the preparation of sulphide dyes by the action of the polysulphide fusion, it appeared of interest to examine the behaviour of dinitro-*ar*-tetrahydro-α-naphthol when subjected to a similar treatment. An equivalent quantity of this compound was substituted for 2:4-dinitrophenol in a technical process for the production of the well-known black sulphide dye (Sulphur Black T, etc.). The product possessed sulphide dyeing properties, but it was tinctorially weak and valueless.

ar-*Tetrahydro-α-naphthol* (I, p. 966).

The *ar*-tetrahydro-α-naphthol required in the following experiment was obtained by the method described by Bamberger and Althausse (*loc. cit.*). *ar*-Tetrahydro-α-naphthylamine was diazotised in the presence of excess of sulphuric acid, the mixture heated until the evolution of nitrogen ceased, and then distilled in a current of steam. The product formed shimmering, silvery plates



melting at 69° (Bamberger and Althausse give 68·5—69°). A further quantity of *ar*-tetrahydro-α-naphthol was prepared by Jacobson and Turnbull's modification (*Ber.*, 1898, **31**, 897) of Bamberger and Bordt's (*Ber.*, 1890, **23**, 215) method, consisting in the reduction of α-naphthol in boiling amyl-alcoholic solution with a large excess of sodium. Of the two methods of preparation, the former is to be preferred, owing to the fact that at least four times as much sodium is required to reduce α-naphthol completely to *ar*-tetrahydro-α-naphthol as is required to reduce α-naphthylamine to *ar*-tetrahydronaphthylamine.

ar-*Tetrahydro-α-naphthol-4-sulphonic Acid* (II, p. 966).

Ten grams of finely powdered *ar*-tetrahydro-α-naphthol were stirred into 20 grams of cold concentrated sulphuric acid. When completely dissolved, the solution was allowed to remain for two days at the ordinary temperature, and the mixture was then diluted with water and filtered from a trace of unsulphonated *ar*-tetrahydro-α-naphthol. The filtrate was neutralised with milk of lime, and the calcium salt, after removal of calcium sulphate, was converted into the sodium salt, evaporated to dryness, and the residue dissolved in a little water and alcohol added until the mixture was opalescent. On allowing to remain, *sodium* ar-*tetrahydro-α-naphthol-4-sulphonate* crystallised in colourless, prismatic needles. The crystals soon effloresce on exposure to air, leaving an amorphous powder. Both the sodium salt and the free sulphonic acid are very readily soluble in water. The sulphonic group is readily hydrolysed by boiling with dilute acids, *ar*-tetrahydro-α-naphthol being regenerated. ar-*Tetrahydro-α-naphthol-4-sulphonic acid* in neutral or alkaline solution does not couple with diazonium salts to form azo-compounds.

A sample of the sodium salt dried at 60° was employed in the following analysis:

0·2288 gave 0·2096 $BaSO_4$. S=12·58.

$C_{10}H_{11}O_4SNa$ requires S=12·80 per cent.

2-*Nitro*-ar-*tetrahydro-α-naphthol-4-sulphonic Acid* (III, p. 966).

Eight grams of *ar*-tetrahydro-α-naphthol were dissolved in 16 grams of cold concentrated sulphuric acid. The solution was allowed to remain for two days, diluted with 25 c.c. of water, cooled in ice, and nitrated with 3·7 c.c. of nitric acid (one molecular proportion, D 1·4) diluted with 8 c.c. of water. The nitrosulphonic acid separated in yellow needles, which were collected, and a further quantity was obtained by adding an excess of hydrochloric acid to the filtrate. The product was recrystallised by dissolving in a little water and adding hydrochloric acid. 2-*Nitro*-ar-*tetrahydro-α-naphthol-4-sulphonic acid* crystallises in long, pale yellow, flat needles melting at 182°, which are readily soluble in water or alcohol. It dissolves in dilute alkalis with a yellow colour, forming very readily soluble salts, and the free sulphonic acid is only reprecipitated by the addition of a large excess of acid. The sulphonic group is readily hydrolysed on boiling with dilute sulphuric acid (1:1).

An air-dried specimen was employed for the following analyses:

0·4158 gave 18·4 c.c. N_2 at 18° and 747 mm. N=5·04.

0·2632 „ 0·2217 $BaSO_4$. S=11·57.

$C_{10}H_{11}O_6NS$ requires N=5·12; S=11·72 per cent.

0·01 required 7·7 c.c. $TiCl_3$ (1 c.c.=0·001556 gram Fe). Calculated as $C_{10}H_9(OH)(SO_3H)\cdot NO_2$=99·5 per cent., that is, 6H required for reduction.

2-*Nitro*-ar-*tetrahydro*-α-*naphthol* (IV, p. 966).

2-Nitro-*ar*-tetrahydro-α-naphthol-4-sulphonic acid was boiled with dilute sulphuric acid (1:1) and distilled in a current of steam. When crystallised from ether, 2-*nitro*-ar-*tetrahydro*-α-*naphthol* forms long, yellow needles melting at 56°, which are readily soluble in organic solvents but sparingly so in water. It is readily volatile with steam and possesses a sweet, pleasant odour.

2-Nitro-*ar*-tetrahydro-α-naphthol dissolves in sodium hydroxide with an orange coloration. The *sodium* salt crystallises from a hot concentrated aqueous solution in orange-red, shimmering plates or needles.

2-Nitro-*ar*-tetrahydro-α-naphthol couples with diazonium compounds, forming azo-dyes. It may be estimated by titration with a standardised diazonium chloride solution:

0·2246 gave 14·1 c.c. N_2 at 18° and 747 mm. N=7·14.

$C_{10}H_{11}O_3N$ requires N=7·25 per cent.

0·01 required 11·6 c.c. $TiCl_3$ (1 c.c.=0·001495 gram Fe). Calculated as $C_{10}H_{10}(OH)\cdot NO_2$=99·6 per cent., that is, 6H required for reduction.

0·3 required 15·4 c.c. *N*/10-*p*-nitrodiazobenzene. Calculated as $C_{10}H_{10}(OH)\cdot NO_2$=99·07 per cent.

4-*Nitro*-ar-*tetrahydro*-α-*naphthol* (VI, p. 966).

Ten grams of *ar*-tetrahydro-α-naphthol were dissolved in sodium hydroxide, the solution being diluted with water to 300 c.c. To this, an aqueous solution of 7·2 grams of sodium nitrite (two molecular proportions) was added, together with 200 grams of ice. One hundred c.c. of 10 per cent. sulphuric acid, contained in a dropping funnel, the end of which dipped below the surface of the liquid, were then slowly run into the mixture with constant agitation. The yellowish-white precipitate was collected and washed with cold water. The major portion dissolved in sodium carbonate solution, and was filtered from a small quantity of a tarry residue. From the filtrate, the product was precipitated by dilute acetic acid.

4-*Nitro*-ar-*tetrahydro*-α-*naphthol* crystallises from dilute alcohol

in yellow needles melting at 163°. It is not volatile with steam. It dissolves in sodium hydroxide with a yellowish-brown colour, and on the addition of excess of alkali the sodium salt crystallises in brown needles. Its salts are more readily soluble in water than those of the isomeric 2-nitro-compound.

4-Nitro-*ar*-tetrahydro-α-naphthol does not couple with diazonium compounds:

0·2432 gave 15·0 c.c. N_2 at 18° and 758 mm. N = 7·12.

$C_{10}H_{11}O_3N$ requires N = 7·25 per cent.

0·0103 required 11·4 c.c. $TiCl_3$ (1 c.c. = 0·001556 gram Fe). Calculated as $C_{10}H_{10}(OH)\cdot NO_2$ = 99·0 per cent., that is, 6H required for reduction.

2:4-*Dinitro*-ar-*tetrahydro-α-naphthol* (V, p. 966).

Twelve grams of *ar*-tetrahydro-α-naphthol were dissolved in 24 grams of cold concentrated sulphuric acid, the solution was allowed to remain for two days, and diluted with 32 c.c. of water. The clear liquid was cooled in ice and nitrated with 14 c.c. of nitric acid (2·5 molecular proportions, D 1·4) diluted with 16 c.c. of water. The 2-nitro-*ar*-tetrahydro-α-naphthol-4-sulphonic acid crystallised in a mass of yellow needles. The mixture was then warmed on the water-bath at 50° until the separated product was insoluble in cold water. The yield was almost theoretical. 2:4-*Dinitro*-ar-*tetrahydro-α-naphthol* crystallises from ether in large, yellow, rhombic prisms melting at 105°. The same substance is obtained by the further nitration of either 2- or 4-nitro-*ar*-tetrahydro-α-naphthol. It is also formed by nitrating diazotetrahydronaphthalene-4-sulphonic acid. It is soluble in organic solvents, sparingly so in hot water, and is slightly volatile with steam. It dissolves in sodium hydroxide with an orange-brown colour, and the *sodium* salt crystallises from the solution in orange needles:

0·2046 gave 20·4 c.c. N_2 at 18° and 764 mm. N = 11·63.

$C_{10}H_{10}O_5N_2$ requires N = 11·76 per cent.

0·01 required 18·8 c.c. $TiCl_3$ (1 c.c. = 0·001495 gram Fe). Calculated as $C_{10}H_9(OH)(NO_2)_2$ = 99·5 per cent., that is, 12H required for reduction.

D. α-*Chloro*-ar-*tetrahydronaphthalene*.

The preparation of 1-bromotetrahydronaphthalene from *ar*-tetrahydro-α-naphthylamine by the Sandmeyer reaction has been described by C. Smith (T., 1904, **85**, 729). Subsequently, Morgan,

Mickletlhwait, and Winfield prepared from it a bromodinitrotetrahydronaphthalene (T., 1904, **85**, 747).

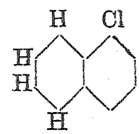
In view of the great reactivity of 4-chloro-1:3-dinitrobenzene, we have now prepared the corresponding chloro- and chlorodinitro-derivatives of tetrahydronaphthalene in order to study the behaviour of the latter compound.

When α-chloronaphthalene in boiling amyl-alcoholic solution is treated with sodium under the same conditions as are employed for the preparation of *ar*-tetrahydro-α-naphthylamine from α-naphthylamine, a mixture is obtained consisting of dihydronaphthalene, tetrahydronaphthalene, and unaltered α-chloronaphthalene. The dihydronaphthalene was identified by conversion into the dibromide, melting at 74° (Bamberger and Lodter, *Ber.*, 1887, **20**, 1706), and the tetrahydronaphthalene, by oxidation to *o*-carboxy-β-phenylpropionic acid, melting at 166° (Bamberger and Kitschelt, *Ber.*, 1890, **23**, 1564). No α-chlorotetrahydronaphthalene was formed by this method. It was therefore prepared directly from *ar*-tetrahydro-α-naphthylamine by Sandmeyer's reaction. The yield of α-chlorotetrahydronaphthalene obtained was not good, as a considerable proportion of *ar*-tetrahydro-α-naphthol and tetrahydronaphthalene was formed simultaneously. No improvement resulted from substituting copper powder for cuprous chloride in this reaction.

The product obtained by nitrating α-chlorotetrahydronaphthalene with two molecular proportions of nitric acid in the cold was largely contaminated with an uncrystallisable resin. Purification was effected by repeated extraction and crystallisation from light petroleum, in which solvent the resinous matter was sparingly soluble. When pure, the product, chlorodinitrotetrahydronaphthalene, crystallised in almost colourless plates or needles melting at 68°. It showed marked differences in behaviour towards amines, etc., from that exhibited by chlorodinitrobenzene. Thus, whilst the latter reacts readily with a hot alcoholic solution of hydrazine hydrate, the chlorodinitrotetrahydronaphthalene remains unaltered. It is also not attacked by aniline or other amines. This inactivity must probably be attributed to sterical hindrance.

On the other hand, both aromatic and alicyclic tetrahydro-α-naphthylamines condense with 4-chloro-1:3-dinitrobenzene, forming two isomeric dinitrophenyltetrahydro-α-naphthylamines. The condensation product in the former case crystallises in red leaflets melting at 134°, and in the latter in golden-yellow plates melting at 121°. Both these products were submitted to the action of the polysulphide fusion. No formation of dye occurred when the condenser method was employed, but sulphide dyes were formed in

each case when the temperature of the fusion was raised to 160—170°. The dye derived from dinitrophenyl-*ar*-tetrahydro-α-naphthylamine gave a bluish-green leuco-compound, whilst the leuco-derivative of the dye derived from dinitrophenyl-*ac*-tetrahydro-α-naphthylamine was olive-green. The dyes were tinctorially weak and dyed cotton grey from a sodium sulphide bath. Presumably condensation, resulting in the formation of a dye, occurs only at the dinitrophenyl end of the molecule in each case.

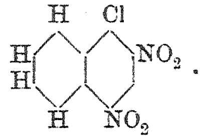
α-Chloro-ar-*tetrahydronaphthalene*, .

Forty grams (1 mol.) of *ar*-tetrahydro-α-naphthylamine, 80 c.c. (2½ mols.) of hydrochloric acid, and 100 c.c. of water were ground into a fine paste and diazotised at 0° by the addition of a concentrated aqueous solution of the requisite amount of sodium nitrite. The clear yellow solution of the diazonium chloride was slowly run into a solution of cuprous chloride, prepared by heating 33 grams of cupric chloride with 15 grams of copper, 133 c.c. of hydrochloric acid, and 28 c.c. of water until colourless. The orange-red coloration produced with each addition of the diazonium salt rapidly disappeared on shaking. The mixture was then raised to the boiling point and distilled in a current of steam. The distillate, which consisted of a yellow, heavy oil, was washed with sodium hydroxide until free from *ar*-tetrahydro-α-naphthol. The insoluble oil was dried over calcium chloride and fractionated. The first fraction, distilling at 204—212°, contained tetrahydronaphthalene, and the second, distilling at 240—245°, contained α-chlorotetrahydronaphthalene. On refractionation, the major portion of the latter boiled at 250°/748 mm. *α-Chloro*-ar-*tetrahydronaphthalene* is a colourless, refractive liquid with an aromatic odour similar to that of chlorobenzene. Unlike α-chloronaphthalene, it does not form a crystalline picrate:

0·2528 gave 0·2164 AgCl. Cl = 21·17.

$C_{10}H_{11}Cl$ requires Cl = 21·32 per cent.

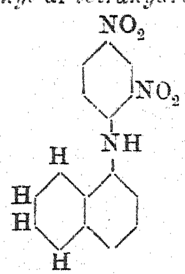
1-*Chloro*-2 : 4-*dinitro*-ar-*tetrahydronaphthalene*,



Six grams of *α*-chloro-*ar*-tetrahydronaphthalene were suspended in 20 c.c. of concentrated sulphuric acid and nitrated with a mixture of 5 c.c. of nitric acid (two molecular proportions, D 1·4) and 10 c.c. of concentrated sulphuric acid at 0°. The mixture was poured on ice, the crude product forming a brown, viscid mass. It was extracted with ether, and the ethereal solution washed with sodium hydroxide until all the yellowish-brown colour was removed. Rosettes of pale yellow needles surrounded by an uncrystallisable resin were deposited from the ethereal solution on keeping. After several crystallisations from light petroleum, the product was obtained in colourless plates or needles melting at 68°. It is readily soluble in organic solvents, is slightly volatile, and has a sweet odour:

0·3426 gave 0·189 AgCl. Cl = 13·70.
0·2044 ,, 19·3 c.c. N_2 at 20° and 754 mm. N = 10·75.
$C_{10}H_9O_4N_2Cl$ requires Cl = 13·84 ; N = 10·91 per cent.
0·01219 required 30·1 c.c. $TiCl_3$ (1 c.c. = 0·001062 gram Fe). Calculated as $C_{10}H_7(NO_2)_2Cl$ = 99·9 per cent., that is, 12H required for reduction.

2 : 4-*Dinitrophenyl*-ar-*tetrahydro*-α-*naphthylamine*,



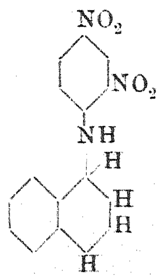
A mixture of 5 grams of *ar*-tetrahydro-*α*-naphthylamine and 6·9 grams of 4-chloro-1 : 3-dinitrobenzene was dissolved in 100 c.c. of alcohol, a hot solution of 4·6 grams of crystallised sodium acetate in a little water was then added, and the mixture boiled for eight hours under a reflux condenser. Condensation proceeds rather slowly. The dinitrophenyl-*ar*-tetrahydro-*α*-naphthylamine separates as it is formed in orange-red needles or plates. The product

crystallises from alcohol in red leaflets melting at 134°. It is readily soluble in acetone, benzene, or acetic acid, but less readily so in boiling alcohol and very sparingly so in cold alcohol. Addition of sodium hydroxide to the yellow alcoholic solution produces a deep red coloration:

0·1644 gave 18·9 c.c. N_2 at 18° and 758 mm. N=13·28.
$C_{16}H_{15}O_4N_3$ requires N=13·42 per cent.

0·01 required 8·4 c.c. $TiCl_3$ (1 c.c.=0·002510 gram Fe). Calculated as $C_{16}H_{15}N(NO_2)_2$=99·87 per cent., that is, 12H required for reduction.

2:4-*Dinitrophenyl*-ac-*tetrahydro*-α-*naphthylamine*,



This compound, prepared in the same manner as the preceding, separates as an oil, which solidifies on cooling. It crystallises from alcohol in golden-yellow plates melting at 121°, which are more readily soluble than the isomeric compound. Addition of sodium hydroxide to the yellow alcoholic solution produces an orange-red coloration:

0·1482 gave 17·1 c.c. N_2 at 18° and 758 mm. N=13·32.
$C_{16}H_{15}O_4N_3$ requires N=13·42 per cent.

0·01 required 8·4 c.c. $TiCl_3$ (1 c.c.=0·002510 gram Fe). Calculated as $C_{16}H_{15}N(NO_2)_2$=99·87 per cent., that is, 12H required for reduction.

In conclusion, we desire to express our thanks to Miss Eva Hibbert, who has kindly carried out the titanous chloride titrations of the nitro-compounds described, and to Messrs. Levinstein, Ltd., who have kindly supplied us with the materials required in this investigation.

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[*Received, October* 18*th*, 1918.]

LXXXVIII.—*The* n-*Butylarylamines. Part I. The Action of* n-*Butyl Chloride on* o- *and* p-*Toluidines.*

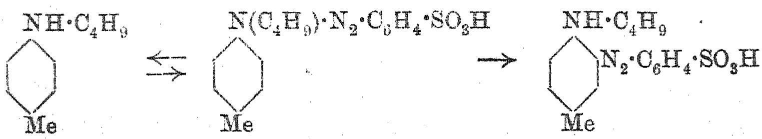
By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

WHILST the methyl- and ethyl-arylamines have been extensively investigated, the study of the members of this series containing larger alkyl groups has hitherto been practically neglected. Thus, in the case of the *n*-butylarylamines, with the exception of the *n*-butylanilines, so far as we are aware, no members of this group have been recorded in the literature. The aniline derivatives were prepared by the action of *n*-butyl chloride on the free base (T., 1917, **111**, 1026), and in the present investigation this reaction has been extended to the butylation of *o*- and *p*-toluidine. This was carried out by a similar method, and also by heating the amine with *n*-butyl alcohol in the presence of a condensing agent. From stereochemical considerations, the increase of the substituting alkyl group from a one- to a four-carbon chain may have a definite effect. In the chain of carbon atoms present in the *n*-butylarylamines, the terminal carbon atoms are probably nearer the nucleus than the corresponding carbon atoms in the lower alkyl derivatives. Consequently, the relation between these atoms and those in the benzene ring may be more intimate than if smaller carbon chains were present, and from the comparative study of these different types of compounds, light may be thrown on the question of ring formation.

When dealing with the alkylation of aniline, it was only necessary to take into account the entering group, but in the case of the toluidines, the influence of the group already in the ring has to be considered. *n*-Butyl chloride reacts with *p*-toluidine, producing both secondary and tertiary arylamines. In the reaction between *n*-butyl chloride and *o*-toluidine, however, it was found that mono-*n*-butyl-*o*-toluidine alone was obtained. Comparative experiments on the methylation and butylation of *o*-toluidine were carried out under conditions in which the dimethyl derivative was obtained. The corresponding di-*n*-butyl derivative, however, was not formed, the mono-*n*-butyl compound being the principal product. The introduction of the *n*-butyl group probably causes an accumulation of carbon atoms in Bischoff's "critical positions," which prevents any reaction between a second molecule of *n*-butyl chloride and the imino-group.

Regarding the two series of mono-*n*-butyltoluidines, on the one hand, with the para-compound, all migration to the para-position

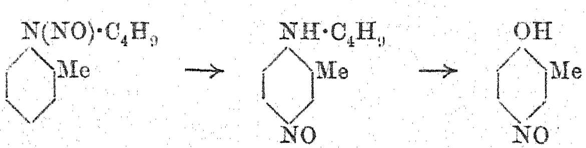
is prevented, as it is already occupied, whilst in the ortho-compound the formation of para-substituted derivatives is possible. Derivatives were therefore prepared of the two series in order to compare their properties. *o-Tolyl-n-butylnitrosoamine* in the presence of alcoholic hydrogen chloride yields the corresponding *p-nitroso*-compound, whilst when the nitrosoamine of *n*-butyl-*p*-toluidine is warmed with alcoholic hydrogen chloride, the nitroso-group is completely removed. Similarly, all attempts to effect a migration of the nitroso-group to the nucleus failed. On the other hand, it was found that by allowing diazotised sulphanilic acid to combine with *n*-butyl-*p*-toluidine (I) in acid solution, a mixture of diazoamino- and *o*-azo-compounds was obtained, namely, *4-methyl-N-n-butyldiazoaminobenzene-4′-sulphonic acid* (II) and *3-p-sulphobenzeneazo-n-butyl-p-toluidine* (III). Under similar conditions,



(I.) (II.) (III.)

n-butylaniline gave almost exclusively the para-compound (this vol., p. 99).

The blue, crystalline *p*-nitroso-compound of *n*-butyl-*o*-toluidine (IV) has the property of forming additive compounds with metallic salts. The dark green, crystalline *cuprichloride* was isolated. By the action of alkali hydroxide on 5-nitroso-*n*-butyl-*o*-toluidine (V), this compound was decomposed, with the formation of *n*-butylamine and 5-nitroso-*o*-cresol, thus proving the migration of the nitroso-group in *o*-tolyl-*n*-butylnitrosoamine to the ring and establishing the orientation of the nitroso-compound.

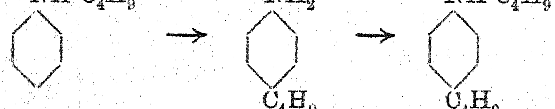


(IV.) (V.)

Di-*n*-butyl-*p*-toluidine is not affected to any appreciable extent by the action of nitrous acid for a short time, consequently the secondary and tertiary amines were separated by the use of this agent, the tertiary amine being recovered unchanged, whilst the secondary amine was obtained from the resulting nitrosoamine by the action of hydrochloric acid or by reduction. Another method available for the separation of the secondary and tertiary *n*-butyl-

p-toluidines depends on the difference in the physical properties of the picrates. The picrate of mono-*n*-butyltoluidine is an oil, whilst that of the di-*n*-butyl compound is a solid which is readily obtained in a crystalline form.

n-Butyl-*p*-toluidine was also obtained by heating *n*-butyl alcohol with *p*-toluidine hydrochloride. At about 140°, the secondary amine was produced, but on increasing the temperature, the yield diminished, and at about 240° no *n*-butyl-*p*-toluidine was isolated. Instead, a primary amine was collected in a fraction boiling between 255° and 270°. The other products consisted of a secondary amine of a higher boiling point, together with some ammonia, and a substance which had an odour resembling that of quinoline. The action of acids changed the latter substance to a resinous material. It is apparent that, even at the temperature employed, the reaction is not a simple one. The butyl group probably enters the nucleus, but the reaction is complicated by the presence of the methyl group which is already in the ring. In order to study this reaction more fully, therefore, it was decided first to investigate the action of *n*-butyl alcohol on aniline hydrochloride before proceeding to the more complex cases of *o*- and *p*-toluidine. The authors have already shown (this vol., p. 102) that *n*-butyl alcohol and aniline hydrochloride, when heated under pressure at a temperature below 200°, furnish mono-*n*-butylaniline (VII). The presence of a primary amine was also shown, and at the time this was assumed to be aniline. It is possible that a small quantity, at least, of a new amine was present. At higher temperatures, the amount of this amine increases. Thus, on heating a mixture of aniline hydrochloride and *n*-butyl alcohol in approximately molecular proportions to 240—280° for six to ten hours, the chief product was identified as p-*amino*-n-*butylbenzene* (VIII). It gives a *sulphate* which is almost insoluble in water. There were higher butylated products, consisting probably for the most part of p-n-*butylamino*-n-*butylbenzene* (IX). This reaction



(VII.) (VIII.) (IX.)

is interesting in that it throws some light on the production of alkyl nuclear substituted arylamines. The production of *p*-amino-*n*-butylbenzene would seem to follow from an intramolecular change of the *n*-butylaniline which is first produced. If this is the case, the reaction is remarkable in that it would indicate an

appreciable change in the stability of the alkyl-substituted anilines as the molecular weight of the alkyl group increases, especially when it is remembered that dimethylaniline may be produced in almost quantitative yield by the action of methyl alcohol on aniline at 220° in the presence of a catalyst. The production of *p*-toluidine from methylaniline is stated to require a temperature of 300°, yet it is possible to obtain *p*-amino-*n*-butylbenzene from aniline hydrochloride and *n*-butyl alcohol at as low a temperature as 200°. These results would indicate that the *n*-butyl group is attached to the nitrogen atom less firmly than is the methyl or ethyl group in corresponding compounds. *n*-Butyl alcohol readily loses water with the production of butylene, and it is possible that butylene, if formed, may react directly with the benzene nucleus with the production of a butylbenzene derivative. The question of the introduction of the *n*-butyl group into the benzene ring is being further investigated.

Experimental.

By heating *p*-toluidine with *n*-butyl chloride, both mono- and di-*n*-butyl-*p*-toluidines were formed. A solution of dry, powdered *p*-toluidine (1 mol.) in *n*-butyl chloride (2·5 mols.) was heated on a sand-bath under reflux until no more *n*-butyl chloride was condensed. This operation usually required sixty to eighty hours. By the addition of a small quantity of a substance such as iodine to the mixture, the time of heating was reduced. The contents of the flask, which were partly solid, contained the hydrochlorides of the mono- and di-alkyl-*p*-toluidines, together with some unchanged *p*-toluidine and *n*-butyl chloride. The unchanged *n*-butyl chloride was distilled off, the residue dissolved in water, treated with sodium carbonate or hydroxide solution, and the separated amines then removed by ether. To the ethereal extract an excess of zinc chloride solution (20 per cent.) was added, when *p*-toluidine zincichloride was precipitated. By washing the precipitate repeatedly with small amounts of ether, the mono- and di-substituted toluidines were removed, and were thus freed from the greater bulk of the *p*-toluidine. The ethereal layer was dried, and on removal of the ether an oil remained which, on distillation, gave crude mono-*n*-butyl-*p*-toluidine at 250—260°, and crude di-*n*-butyl-*p*-toluidine at above 260°.

Pure mono-*n*-butyl-*p*-toluidine was obtained by reducing its nitrosoamine with zinc dust and hydrochloric acid. The crude product (20 grams) was dissolved in a solution of 40 c.c. of concentrated hydrochloric acid in 100 c.c. of water, and then cooled

in ice. A slight excess of concentrated sodium nitrite solution was added to the cold mixture, when the nitrosoamine was formed, which was removed by extraction with ether. The ethereal extract was washed with alkali hydroxide and dried over potassium carbonate. The *p*-tolyl-*n*-butylnitrosoamine (20 grams), freed from ether, was mixed with concentrated hydrochloric acid (90 grams), and zinc dust gradually added in small amounts until an excess was present, the mixture being then heated on the water-bath for a short time. Excess of zinc dust was removed from the mixture by filtration, the zinc being washed several times with small amounts of absolute alcohol. The filtrate was acidified with hydrochloric acid and the alcohol removed by distillation. *n*-Butyl-*p*-toluidine was obtained from the acid residue by adding excess of sodium hydroxide solution, followed by ether extraction or steam distillation. The amine obtained in this manner usually contained a small quantity of substances which on distillation gave free ammonia. Traces of hydrazine might be produced during the reduction, and would be present in the amine. These impurities were removed by heating an ethereal solution of the crude *n*-butyl-*p*-toluidine with yellow mercuric oxide in the presence of alcohol under reflux. By using sodium hyposulphite for the reduction of the nitrosoamine in aqueous suspension or in aqueous-alcoholic solution, the greater part of the nitrosoamine was recovered unchanged.

The effect of heating the nitrosoamine with an excess of an *n*-butyl-alcoholic solution of hydrogen chloride was also investigated. On gently warming, a vigorous action ensued, oxides of nitrogen being evolved. Heating on the water-bath for six hours completed the reaction. Alcohol and water were distilled off, and, on keeping, the hydrochloride of the secondary amine crystallised out. This was purified either by boiling with animal charcoal followed by recrystallisation with water, or by converting it into the free base and passing dry hydrogen chloride into the benzene solution, when, on cooling, crystals of n-*butyl*-p-*toluidine hydrochloride* separated. These were collected and well washed with small amounts of cold benzene, when the hydrochloride was obtained as a white powder, which crystallised from alcohol in colourless, long, transparent needles or flattened prisms melting at 150—151°. By slow evaporation of the alcohol, crystals up to 5 cm. in length were obtained:

0·1988 gave 12·2 c.c. N_2 at 17° and 759 mm. N = 7·21.*
0·1116 „ 0·0804 AgCl. Cl = 17·82.

$C_{11}H_{17}N,HCl$ requires N = 7·02; Cl = 17·76 per cent.

* The nitrogen in every estimation was measured over 40 per cent. potassium hydroxide solution. Pressures corrected for vapour tension are recorded.

The hydrochloride is readily soluble in alcohol, water, or chloroform, less readily so in warm benzene or amyl acetate, sparingly so in cold benzene, and insoluble in ether or light petroleum.

n-*Butyl*-p-*toluidine*, obtained from the hydrochloride by the action of alkali hydroxide and extraction in the ordinary way, is an almost colourless oil boiling at 264—265°/766 mm. and miscible with most organic solvents. It distils in a current of steam:

0·1036 gave 0·3062 CO_2 and 0·0998 H_2O. C=80·60; H=10·70.
0·1043 ,, 7·95 c.c. N_2 at 20·5° and 751 mm. N=8·76.
$C_{11}H_{17}N$ requires C=80·91; H=10·50; N=8·58 per cent.

A hot alcoholic solution of *n*-butyl-*p*-toluidine, when treated with an excess of an alcoholic solution of oxalic acid, gave a precipitate of the sparingly soluble n-*butyl*-p-*toluidine oxalate*. It crystallises from hot alcohol in white, shining plates melting at 185°:

0·1870 gave 0·0410 CaO. $C_2H_2O_4$=35·20.
$C_{11}H_{17}N,C_2H_2O_4$ requires $C_2H_2O_4$=35·55 per cent.

The *picrate* was obtained as a viscous, red oil which did not readily solidify.

Aceto-n-*butyl*-p-*toluidide*.—The acetyl derivative was prepared by mixing the amine (7 grams) with three times its weight of acetic anhydride in the presence of a small quantity of zinc chloride. The mixture at first became very warm, and after the first reaction had subsided, the solution was heated on a sand-bath for half an hour to complete the acetylation. On pouring into water and extracting with ether, the *acetyl* compound separated from the ethereal solution as a very pale yellow, refractive oil which distilled at 294—295°/769 mm.:

0·2000 gave 12·35 c.c. N_2 at 19·3° and 754 mm. N=7·16.
$C_{13}H_{19}ON$ requires N=6·83 per cent.

Benzo-n-*butyl*-p-*toluidide*.—The *benzoyl* derivative, prepared by the Schotten-Baumann reaction, is a very viscous, pale yellow oil, distilling apparently unchanged at a temperature above 380° under the ordinary pressure:

0·3011 gave 12·90 c.c. N_2 at 18·8° and 746 mm. N=4·92.
$C_{18}H_{21}ON$ requires N=5·24 per cent.

p-*Tolyl*-n-*butylnitrosoamine*.—The crude nitrosoamine, prepared as above, was well washed first with dilute hydrochloric acid, then with sodium hydroxide solution, and finally with water. Distillation in a current of steam gave the nitrosoamine as a pale yellow oil having a slight red tinge:

0·1829 gave 23·7 c.c. N_2 at 18° and 735 mm. N=14·70.

$C_{11}H_{16}ON_2$ requires N=14·58 per cent.

The compound is practically insoluble in water, but soluble in most organic solvents. It is denser than water, readily volatile in a current of steam, and gives Liebermann's nitroso-reaction. By the action of an alcoholic solution of hydrogen chloride or by the action of sulphuric acid on its ethereal solution, no formation of nitrosoalkyltoluidine was observed.

By reducing the nitrosoamine in the cold with zinc dust and acetic acid, a mixture of bases was obtained containing some hydrazine derivative. Although *as-p*-tolyl-*n*-butylhydrazine has not been isolated, there is evidence that it is produced by the action of cold hydrochloric or acetic acid and zinc dust on *p*-tolyl-*n*-butylnitrosoamine. The amines are separated as hydrochlorides, and any *n*-butyl-*p*-toluidine hydrochloride produced is precipitated by cold benzene, in which it is only sparingly soluble; the dark solution, after removing the benzene, has reducing properties. By boiling under reflux an alcoholic or ethereal-alcoholic solution of the amine with mercuric oxide, metallic mercury is obtained. An aqueous solution of the hydrochloride reduces Fehling's solution slowly on boiling. If the amine is distilled under the ordinary pressure, ammonia is liberated, and the distillate darkens very rapidly in the air. These properties are in accordance with the assumption that a monoalkylhydrazine is present.

Di-n-*butyl*-p-*toluidine*.

From the fraction of the oil, boiling at above 260°, obtained by the action of *n*-butyl chloride on *p*-toluidine, by repeated fractional distillation, a pale yellow, refractive liquid, identified as the dialkylamine, was obtained which boiled at 282—284°/764 mm. It was also obtained pure from the crude mixture of mono- and di-*n*-butyl-*p*-toluidine by the following procedure. The mixed alkylamines were dissolved in excess of dilute hydrochloric acid and treated with nitrous acid. The nitrosoamine of the secondary base separated as an oil, and was removed by ether. The residue, after being heated for half an hour on the water-bath and then rendered alkaline, gave *di*-n-*butyl*-p-*toluidine*. It has only a faint odour. On exposure to light and air, the practically colourless oil slowly turns to a claret or dark red colour:

0·0596 gave 0·1799 CO_2 and 0·0618 H_2O. C=82·33; H=11·52.
0·1940 ,, 11·15 c.c. N_2 at 22·1° and 751 mm. N=6·57.

$C_{15}H_{25}N$ requires C=82·12; H=11·49; N=6·39 per cent.

Di-n-*butyl*-p-*toluidine* is soluble in the common organic solvents,

including acetic acid, and also in concentrated hydrochloric acid. When a solution of the base in an excess of dilute hydrochloric acid was treated with an aqueous solution of potassium ferrocyanide, a white precipitate of the *ferrocyanide* was obtained:

0·1000 gave 0·0174 Fe_3O_4. Fe=12·6.

$C_{15}H_{25}N,H_4Fe(CN)_6$ requires Fe=12·8 per cent.

It is a white powder, practically insoluble in water, ether, or alcohol. On exposure to air and light, the top layer very slowly turns green.

The *picrate* was obtained by shaking the crude amine with an excess of aqueous picric acid solution. It crystallises from a mixture of ether and light petroleum in pale yellow, rectangular crystals melting at 109—110°:

0·0706 gave 8·1 c.c. N_2 at 26° and 745·8 mm. N=12·85.

$C_{15}H_{25}N,C_6H_3O_7N_3$ requires N=12·50 per cent.

Titration with Titanous Chloride.—0·0104 required 17·3 c.c. $TiCl_3$ (1 c.c.=0·001351 gram Fe). Calculated as

$C_{15}H_{25}N,C_6N_3O_7N_3$=100·2 per cent.

It is soluble in alcohol or acetone, moderately so in ether, and very sparingly so in light petroleum.

n-*Butyl-o-toluidine.*

By the action of *n*-butyl chloride on *o*-toluidine in the manner described in the case of *p*-toluidine, n-*butyl-o-toluidine* was prepared. By fractionating the oil obtained after removing most of the *o*-toluidine as the sparingly soluble zincichloride, *n*-butyl-*o*-toluidine was isolated as a colourless oil boiling at 258—260°/771 mm.

It is similar in general properties to the *n*-butyl-*p*-toluidine, has a faint, pleasant odour, and is lighter than water:

0·1360 gave 9·85 c.c. N_2 at 21° and 754·2 mm. N=8·35.

$C_{11}H_{17}N$ requires N=8·58 per cent.

As there was no fraction boiling above 260°, it would appear that di-*n*-butyl-*o*-toluidine is not formed under these conditions, and accordingly *n*-butyl-*o*-toluidine was heated on a sand-bath under reflux with a large excess of *n*-butyl chloride for ten days. Even after this period, it was not possible to isolate any di-*n*-butyl-*o*-toluidine, the product being for the most part unchanged mono-*n*-butyl-*o*-toluidine.

The monoalkyl compound gives an almost colourless *acetyl* derivative, which is an oil:

0·2044 gave 12·1 c.c. N_2 at 23° and 749·3 mm. N=6·73.
$C_{13}H_{19}ON$ requires N=6·83 per cent.

By the action of sodium nitrite solution on n-*butyl-o-toluidine* dissolved in hydrochloric acid, *o-tolyl*-n-*butylnitrosoamine* was obtained as a yellow oil, which is volatile in a current of steam and has a characteristic odour:

0·1038 gave 13·0 c.c. N_2 at 21° and 753·8 mm. N=14·42.
$C_{11}H_{16}ON_2$ requires N=14·58 per cent.

5-Nitroso-n-*butyl-o-toluidine Hydrochloride*.—By the action of alcoholic hydrogen chloride on the nitrosoamine in ethereal solution, the hydrochloride of the nitroso-derivative was obtained in good yield as a pale, greenish-yellow powder. On heating, it decomposed with a feeble explosion at 136°, darkening at a few degrees below that temperature:

0·1274 gave 0·0815 AgCl. Cl=15·82.
$C_{11}H_{16}ON_2,HCl$ requires Cl=15·51 per cent.

The *hydrochloride* is readily soluble in water, giving an intense yellow solution. It is also readily soluble in alcohol and practically insoluble in ether. The addition of a dilute solution of ammonia to an aqueous solution of the hydrochloride resulted in the precipitation of *5-nitroso*-n-*butyl-o-toluidine*. Extraction with ether and removal of the solvent furnished the base as a green oil, which quickly solidified to a blue, crystalline compound. From a mixture of ether and light petroleum, it crystallised in masses of deep blue needles melting at 50°:

0·1448 gave 18·8 c.c. N_2 at 25° and 749·4 mm. N=14·67.
$C_{11}H_{16}ON_2$ requires N=14·58 per cent.

It is soluble in benzene, methyl alcohol, or acetone, moderately so in carbon disulphide, sparingly so in ether, and practically insoluble in light petroleum.

5-Nitroso-n-*butyl-o-toluidine Cuprichloride*.—The nitroso-base (2·5 mols.), dissolved in a small amount of hot methyl alcohol, was added to a hot aqueous methyl-alcoholic solution of cupric chloride (1 mol.). The mixture, on keeping overnight, deposited dark green crystals of the *cuprichloride*:

0·1573 gave 0·0837 AgCl. Cl=13·2.
$(C_{11}H_{16}ON_2)_2,CuCl_2$ requires Cl=13·5 per cent.

The nitroso-compound was decomposed by alkali hydroxide as follows. It was added to an excess of 10 per cent. sodium hydroxide solution, and steam passed into the solution. The colour rapidly became reddish-brown, and at the same time ammoniacal vapours were evolved, which were absorbed in hydrochloric acid

(20 per cent.). After the steam had passed in for about ten minutes, the residue in the flask was filtered, the filtrate slightly acidified with dilute sulphuric acid, and finally extracted with ether. From the ethereal solution, crystals were obtained which melted at 132—133°.

The compound had properties similar to those of 5-nitroso-*o*-cresol, and the hydrochloric acid solution was shown to contain *n*-butylamine. This decomposition confirmed the constitution of the nitroso-compound.

Action of n-*Butyl Alcohol on Primary Arylamine Salts.*

Pure *p*-toluidine hydrochloride (10 grams) was heated in a sealed tube with *n*-butyl alcohol (7·5 grams) at an initial temperature of 220°, gradually rising to 260°. The heating was stopped after seven to eight hours. On slowly cooling the tube, its contents partly solidified. In addition to the crystals, a dark brown, viscid liquid was present, and also a gas, which had an odour resembling that of butylene, burning with a smoky flame. On rendering the contents of the tube alkaline, an ammoniacal odour was perceived. On extraction with ether followed by distillation, the main fractions boiled between 220° and 300°, a residue being left in the flask. From the fraction boiling at 220—230°, a small amount of a substance was obtained of characteristic odour, which was insoluble in dilute hydrochloric acid solution and appeared to be resinified by concentrated hydrochloric acid.

The fraction boiling at 255—270° contained a considerable amount of a primary amine, with only a small quantity of a secondary amine. It was evident that the production of *n*-butyl-*p*-toluidine had not been realised, but that a more complicated reaction had occurred. The evidence points to the production of an aminobutyltoluene, and in order to study this type of reaction, the *p*-toluidine was substituted by aniline.

Aniline hydrochloride (1 mol.) was heated at 240—260° in a sealed tube with *n*-butyl alcohol (1·3 mols.) for seven to eight hours. On opening the cold tube, there was a slight pressure of gas, and the contents of the tube had partly crystallised. The product was rendered alkaline and distilled. A fraction boiling at 255—265° was obtained, which was characterised by yielding an insoluble *sulphate*, from which was prepared a primary amine boiling at 258—260°/750 mm. Its properties indicate that it is an *aminobutylbenzene*:

0·0745 gave 6·20 c.c. N_2 at 20·2° and 740·9 mm. N=9·45.

$C_{10}H_{15}N$ requires N=9·39 per cent.

It is a pale yellow oil which slowly becomes red. It is practically insoluble in water, and gives no characteristic colours with bleaching powder solution or with chromic acid. It can be diazotised, and the resulting diazonium salt combines with alkaline β-naphthol to yield a red *azo*-compound, which dissolves in concentrated sulphuric acid with a purple-red colour. This primary amine is being further studied.

Combination of Mono-n-*butyl*-p-*toluidine with Diazotised Sulphanilic Acid.*

Sulphanilic acid (2·5 grams) was diazotised, and the solution slowly added to a solution containing a similar weight of mono-*n*-butyl-*p*-toluidine in 30 grams of glacial acetic acid. The mixture rapidly became blood-red, but, after eight hours' shaking and then allowing the solution to remain for forty-eight hours, it was very dark in colour, whilst dark brown needles had separated. These were collected, and as they were very soft and viscid, they were kept for a few days in a vacuum desiccator over potassium hydroxide, when they were obtained as a hard, red mass of crystals. After being washed with water, in which they are only sparingly soluble, they were recrystallised from aqueous alcohol, and obtained in large, red, crystalline plates.

From the free acid, the *potassium* salt was prepared by adding a solution of potassium hydroxide (slightly more than 1 mol.) in methyl alcohol to a concentrated solution of the acid in absolute methyl alcohol. The potassium salt was precipitated as a bright red powder soluble in water, but sparingly so in absolute methyl alcohol:

0·1794 gave 0·0408 K_2SO_4. K=10·2.

$C_{17}H_{20}O_3N_3SK$ requires K=10·1 per cent.

The reduction of the crude potassium salt by means of sodium hyposulphite in warm aqueous solution gave, on making alkaline with sodium hydroxide, an oily layer, which became dark blue on keeping. The product contained a secondary amine, as shown by the action of nitrous acid, which gave *p*-tolyl-*n*-butylnitrosoamine. In addition, a diamine was present, probably an amino-*n*-butyl-*p*-toluidine, which was readily oxidised to a blue compound. The formation of the above two reduction products indicates that the product of combination contains the azo- and the diazoamino-compounds.

The pure *diazoamino*-compound was obtained by allowing the diazotised solution of sulphanilic acid to combine with the amine

in alcoholic solution under the following conditions. *n*-Butyl-*p*-toluidine (4·5 grams) was dissolved in alcohol (250 c.c.) and treated with a diazotised solution of sulphanilic acid (5 grams). The solution was shaken, and as the combination proceeded the colour changed to red. The addition of saturated sodium acetate solution, followed by removal of the alcohol on the water-bath, gave yellow crusts of the *sodium* salt of *4-methyl-*N-n-*butyldiazoaminobenzene-4'-sulphonic acid* in a crude form mixed with sodium acetate. The purified compound is sparingly soluble in concentrated sodium acetate solution, but soluble in water. The free diazoamino-compound was prepared by treating the aqueous solution of the sodium salt with a slight excess of dilute sulphuric acid (1 mol.) in the presence of an excess of ether, when the pale red, free acid was dissolved by the ethereal layer. Treatment of an absolute alcoholic solution of the acid with a slight excess of alcoholic potassium hydroxide gave a pale red precipitate of the *potassium* salt:

0·0775 gave 0·0180 K_2SO_4. K=10·4.

$C_{17}H_{20}O_3N_3SK$ requires K=10·1 per cent.

Reduction of the potassium salt in alkaline solution by means of hyposulphite gave a secondary amine which was isolated in the form of its hydrochloride. The amine was identified as *n*-butyl-*p*-toluidine.

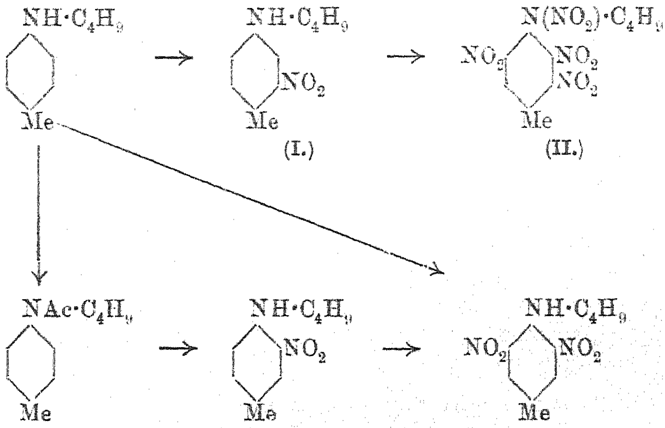
[*Received November 7th*, 1918.]

LXXXIX.—*The* n-*Butylarylamines. Part II. Nitration of Mono- and Di*-n-*butyl*-p-*toluidines.*

By JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM.

THE authors have made a study of the products of nitration of mono- and di-*n*-butyl-*p*-toluidine, which bases are described in the preceding paper. In the presence of an excess of sulphuric acid and the theoretical amount of nitric acid for the introduction of one nitro-group, the production of *2-nitro*-n-*butyl*-p-*toluidine* (I) proceeded smoothly, the pure compound being readily obtained from the recrystallised hydrochloride or sulphate. A more readily soluble portion, after precipitating the greater part of the 2-nitro-compound as the hydrochloride, contained small amounts of

another nitro-compound. By using more than the calculated amount of nitric acid for the introduction of one nitro-group, a small amount of a white solid was isolated, crystallising in white needles melting at 122—125°.

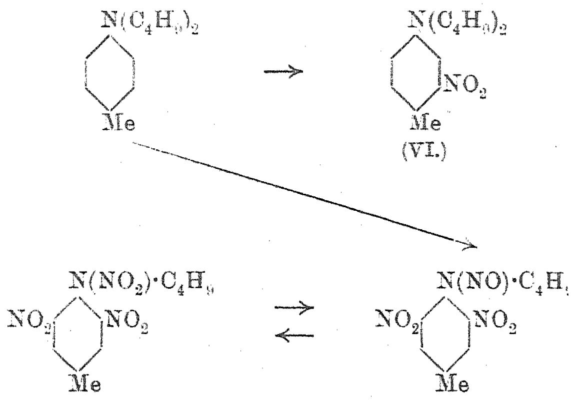


(I.) (II.) (III.) (IV.) (V.)

When aceto-*n*-butyl-*p*-toluidide (III) was nitrated in acetic acid solution by means of fuming nitric acid, a nitroacetyl compound was obtained differing from that produced by the action of acetic anhydride on the 2-nitro-derivative. Hydrolysis by means of sulphuric acid (60 per cent.) yielded 3-*nitro*-n-*butyl*-p-*toluidine* (IV), which gave a soluble sulphate and hydrochloride.

By the action of nitric acid on a solution of the amine in glacial acetic acid, the chief product was 3:5-*dinitro*-n-*butyl*-p-*toluidine* (V), which is an orange-red, crystalline solid melting at 53—54°. Under more vigorous conditions, a pale yellow compound was formed, identical with that obtained by the action of nitrous acid on the dinitro-derivative, and was consequently the nitrosoamine, which, by further action of nitric acid, was converted into the corresponding nitroamine. When 2-nitro-*n*-butyl-*p*-toluidine was nitrated either by fuming nitric acid or by a mixture of sulphuric and nitric acids, a *trinitro*-p-*tolyl*-n-*butylnitroamine* (II) was produced, the nitro-groups being probably in the 2:3:5-positions.

The nitration of di-*n*-butyl-*p*-toluidine in sulphuric acid by means of the theoretical amount of nitric acid yielded 2-*nitrodi*-n-*butyl*-p-*toluidine* (VI), and nitric acid in glacial acetic acid gave the same nitrosoamine as was obtained from the monoalkyltoluidine under similar conditions, namely, 3:5-*dinitro*-p-*tolyl*-n-*butylnitrosoamine*.



(VI.) (VII.) (VIII.)

It was considered that an examination of the products of nitration of *n*-butyl-*p*-toluidine would throw some light on the mechanism of nitration. With a small amount of nitric acid, a dinitro- and a mononitro-compound were obtained; on the other hand, with an excess of nitric acid, varying amounts of dinitro-*p*-tolyl-*n*-butylnitroamine and nitrosoamine were produced, the amount of the nitroamine increasing with the temperature. If the nitration proceeded with the intermediate product of nitroamines, some mononitro-*p*-tolyl-*n*-butylnitroamine should be obtained, as compounds of this type are relatively stable towards nitric acid (Pinnow, *Ber.*, 1897, **30**, 835).

When *p*-tolyl-*n*-butylnitrosoamine was nitrated by a solution of nitric acid in acetic acid, or by means of concentrated nitric acid, dinitro-*p*-tolyl-*n*-butylnitrosoamine was the usual product, the corresponding nitroamine only being produced by the further action of nitric acid. The reverse action, namely, the formation of the nitrosoamine from the nitroamine, can also be brought about. The production of the dinitroamine has not been observed, whilst the amount of dinitronitroamine formed was small and depended on the temperature at which the nitration was carried out, the amount increasing with the temperature. The results obtained by nitrating *n*-butyl-*p*-toluidine, and also *p*-tolyl-*n*-butylnitrosoamine, under different conditions would appear to be most readily explained by assuming that the nitration proceeds directly without the intermediate formation of a nitroamine.

EXPERIMENTAL.

2-*Nitro*-n-*butyl*-p-*toluidine*.

A solution of *n*-butyl-*p*-toluidine (10 grams) in concentrated sulphuric acid (40 grams) was cooled to $-5°$, and the calculated amount of nitric acid (D 1·42 : 1 mol.) dissolved in three times its weight of concentrated sulphuric acid was added, the temperature being kept below 10°. The product was allowed to remain for some time, and then poured on ice, when the sulphate of the mononitro-derivative separated as a yellow, crystalline solid. This was collected, dried, dissolved in water, and the solution neutralised with sodium hydroxide or ammonia solution, when 2-*nitro*-n-*butyl*-p-*toluidine* separated as a red oil. It was purified by preparing the sulphate and regenerating the base as described above:

0·1328 gave 15·10 c.c. N_2 at 16·6° and 756·0 mm. N=13·33.

$C_{11}H_{16}O_2N_2$ requires N=13·46 per cent.

This nitro-compound is soluble in most of the organic solvents. It is characterised by the ease with which it forms well-defined salts sparingly soluble in excess of the free acid used to precipitate them. The *sulphate* was obtained pure by recrystallising the crude sulphate from hot absolute alcohol and washing with a mixture of alcohol and ether. It forms white, shining plates darkening at 147—149° and melting at 152°:

0·1212 gave 9·6 c.c. N_2 at 18·1° and 752 mm. N=9·19.

$C_{11}H_{16}O_2N_2,H_2SO_4$ requires N=9·15 per cent.

The sulphate is easily hydrolysed by water; it is soluble in absolute alcohol or glacial acetic acid, but sparingly so in moderately concentrated sulphuric acid. The filtrate from the crude sulphate still contained an appreciable amount of the nitro-compound, which was obtained as the free base by rendering the solution alkaline and extracting with ether. The *hydrochloride* was prepared by treating the purified nitro-compound with an excess of concentrated hydrochloric acid. The precipitate was collected and dried in a vacuum desiccator over potassium hydroxide, when the salt was obtained as a white, crystalline compound which was readily hydrolysed by water. The hydrochloride was purified for analysis by crystallisation from absolute alcohol:

0·0738 gave 0·0438 AgCl. Cl=14·68.

$C_{11}H_{16}O_2N_2,HCl$ requires Cl=14·50 per cent.

The *hydrobromide* was prepared by adding aqueous hydrobromic acid to the base, when it was obtained as a crystalline precipitate. This salt is more readily soluble than the corresponding hydro-

chloride, and is readily hydrolysed by water. It crystallises from alcohol in white, shining plates.

2-Nitroaceto-n-butyl-p-toluidide was prepared by warming 2-nitro-*n*-butyl-*p*-toluidine with an excess of acetic anhydride in the presence of a very small quantity of concentrated sulphuric acid or of fused zinc chloride. It was obtained as a yellow oil, which solidified to a mass of pale yellow needles melting at 48—49°:

0·1032 gave 9·9 c.c. N_2 at 25° and 748·3 mm. N=10·82.
$C_{13}H_{18}O_3N_2$ requires N=11·20 per cent.

2-Nitro-p-tolyl-n-butylnitrosoamine.

Two grams of 2-nitro-*n*-butyl-*p*-toluidine sulphate were triturated with 10 c.c. of glacial acetic acid, the solution was then diluted by the addition of crushed ice, and a slight excess of the calculated amount of sodium nitrite solution gradually added. The mixture was poured into an excess of water, followed by extraction with ether. After washing the ethereal solution with sodium hydroxide solution and drying, the nitrosoamine was obtained as a pale yellow oil:

0·1028 gave 15·65 c.c. N_2 at 19·2° and 759 mm. N=17·77.
$C_{11}H_{15}O_3N_3$ requires N=17·72 per cent.

2-Nitro-p-tolyl-n-butylnitrosoamine is soluble in most organic solvents, sparingly so in light petroleum, and insoluble in water. It gives Liebermann's nitroso-reaction.

3-Nitro-n-butyl-p-toluidine.

This compound could not be conveniently prepared by direct nitration, consequently it was obtained by the hydrolysis of the corresponding 3-nitroaceto-*n*-butyl-*p*-toluidide. The latter compound was prepared by the following method. To a solution of aceto-*n*-butyl-*p*-toluidide (4 grams) dissolved in six times its weight of glacial acetic acid, nitric acid (D 1·5: 30 grams) was added slowly, the temperature being kept below 20°. After the mixture had remained for some days, it was poured into a mixture of ice and water, and the free acid neutralised with sodium carbonate solution. A brownish-yellow oil was obtained, which solidified after remaining for a few hours in the ice-chest. After being crystallised several times from aqueous alcohol, it separated in pale yellow, square crystals melting at 68°:

0·0786 gave 7·45 c.c. N_2 at 19·1° and 750 mm. N=10·93.
$C_{13}H_{18}O_3N_2$ requires N=11·20 per cent.

Titration with Titanous Chloride.—0·0096 required 9·5 c.c. $TiCl_3$ (1 c.c. = 0·001351 gram Fe). Calculated as $C_{13}H_{18}O_3N_2$ = 99·8 per cent.

3-*Nitroaceto*-n-*butyl*-p-*toluidide* is very readily soluble in ethyl acetate or benzene, moderately so in ether or alcohol, but practically insoluble in light petroleum or water.

3-*Nitro*-n-*butyl*-p-*toluidine* was prepared by gently boiling the nitroacetyl compound with twenty-five times its weight of sulphuric acid (D 1·47). The colour became deeper, and finally, after about thirty minutes' heating, it was almost black. After remaining overnight, the nitro-derivative was obtained by neutralising with sodium carbonate solution and extraction with ether, when it was left as a red oil on removing the solvent:

0·1568 gave 18·25 c.c. N_2 at 20° and 749 mm. N = 13·37.

$C_{11}H_{16}O_2N_2$ requires N = 13·46 per cent.

Titration with Titanous Chloride.—0·02429 requires 20·0 c.c. $TiCl_3$ (1 c.c. = 0·00196 gram Fe). Calculated as $C_{11}H_{16}O_2N_2$ = 100·2 per cent.

The substance is distinguished from the corresponding 2-nitro-compound in giving a more readily soluble sulphate and hydrochloride.

3 : 5-*Dinitro*-n-*butyl*-p-*toluidine*.

Mono-*n*-butyl-*p*-toluidine (5 grams) was dissolved in ten times its weight of glacial acetic acid, and a solution of nitric acid (D 1·5: 30 grams) in glacial acetic acid (10 grams) added slowly. After a few hours, the mixture was poured on ice, when a red oil separated which, after extracting with ether and removal of the solvent, slowly acidified in the ice-chest to a mass of red needles. The compound crystallised from methyl alcohol in orange-red needles melting at 53—54°:

0·0713 gave 10·3 c.c. N_2 at 20° and 737 mm. N = 16·32.

$C_{11}H_{15}O_4N_3$ requires N = 16·60 per cent.

Titration with Titanous Chloride.—0·0118 requires 16·3 c.c. $TiCl_3$ (1 c.c. = 0·001914 gram Fe). Calculated as $C_{11}H_{15}O_4N_3$ = 100 per cent.

It is insoluble in water, moderately soluble in light petroleum or cold methyl alcohol, and readily so in acetone, ether, benzene, or carbon tetrachloride.

On warming 3 : 5-dinitro-*n*-butyl-*p*-toluidine (1 mol.) with acetic anhydride (2 mols.) and one drop of sulphuric acid, and then neutralising with sodium carbonate solution, 3 : 5-*dinitroaceto*-n-*butyl*-p-*toluidide* was obtained as a dark-coloured oil which slowly

solidified to a dark, crystalline mass. By extraction with aqueous alcohol and repeated crystallisation from a mixture of light petroleum and acetone, it was obtained in clusters of very pale yellow needles melting at 55—56°:

0·0704 gave 8·8 c.c. N_2 at 25° and 753·4 mm. N = 14·20.

$C_{13}H_{17}O_5N_3$ requires N = 14·24 per cent.

Titration with Titanous Chloride.—0·0109 requires 18·5 c.c. $TiCl_3$ (1 c.c. = 0·001351 gram Fe). Calculated as $C_{13}H_{17}O_5N_3$ = 100·8 per cent.

It is readily soluble in the usual solvents, sparingly so in light petroleum, and insoluble in water. The addition of a warm concentrated solution of potassium hydroxide to an alcoholic solution gives a purple coloration at the junction of the two liquids.

3:5-*Dinitro*-p-*tolyl*-n-*butylnitrosoamine* (VIII, p. 987).

3:5-Dinitro-*n*-butyl-*p*-toluidine (1 mol.) was dissolved in ten times its weight of glacial acetic acid, the solution cooled to 5°, and a solution of nitrous acid in acetic acid added. On allowing to remain for one hour and pouring on ice, the nitrosoamine separated as a yellow solid. It crystallised from aqueous methyl alcohol in pale yellow plates melting at 56—57°:

0·0708 gave 12·45 c.c. N_2 at 25·6° and 743·4 mm. N = 19·67.

$C_{11}H_{14}O_5N_4$ requires N = 19·86 per cent.

The nitrosoamine is insoluble in water, but readily soluble in most of the common organic solvents except light petroleum, in which it is only sparingly soluble. It responds to Liebermann's test for nitrosoamines. It is acted on by alkali hydroxides, a purple colour being produced, which changes to deep red. Light changes the colour from yellow to red. This nitrosoamine is also readily obtained by the nitration of *n*-butyl-*p*-toluidine under more vigorous conditions than those required for the production of the dinitro-compound. The nitration of *n*-butyl-*p*-toluidine as described above furnishes the nitrosoamine even if the mixture is allowed to remain for three weeks. During this time the colour changes, gradually becoming a darker red after a few hours, until it is almost black; after this the colour gradually becomes paler again, finally a pale yellow. The nitration was repeated, using less acetic acid, so that the mixture became warm. In this case, the change from the dark colour to the pale yellow took place rapidly, and, after twelve hours, the nitrosoamine was precipitated by pouring on ice. It was also prepared by nitrating *p*-tolyl-*n*-butylnitrosoamine in glacial acetic acid. A solution of the nitrosoamine

(3·3 grams) in glacial acetic acid (20 grams) was cooled in a freezing mixture, and a solution of nitric acid (D 1·5 : 22 grams) in glacial acetic acid (10 grams) added slowly. The mixture was allowed to remain until the dark colour had changed to a pale yellow, when the product was found to be chiefly 3 : 5-*dinitro*-p-*tolyl*-n-*butylnitrosoamine*, and was very pale yellow. When this nitration was repeated, using a larger amount of nitric acid and allowing the mixture to become hot, the product had a considerably higher melting point than the nitrosoamine. Its manner of preparation and its reactions show that it is 3 : 5-dinitro-*p*-tolyl-*n*-butylnitroamine.

Under the following conditions, the compound can be produced in good yield. *p*-Tolyl-*n*-butylnitrosoamine (10 grams) was dissolved in glacial acetic acid (30 grams), and nitric acid (80 grams) added slowly with cooling, the temperature being kept below 30°. When the dark red colour of the solution had given place to a pale yellow, the mixture was warmed to 80—90° for an hour. On pouring into water, 3 : 5-dinitro-*p*-tolyl-*n*-butylnitroamine was precipitated as a white solid. After several crystallisations from aqueous alcohol (80 per cent.), it formed faintly yellow needles melting at 95°.

The action of fuming nitric acid on *p*-tolyl-*n*-butylnitrosoamine is extremely vigorous, but it was found possible to nitrate this compound by using a weaker acid at first and completing the reaction with the strong acid (D 1·5). To 11·4 grams of the nitrosoamine, 45 grams of nitric acid (D 1·4) were added gradually with cooling. After the mixture had remained for a short time, 60 c.c. of nitric acid (D 1·5) were added, and the mixture was then heated at 80—100° for about five minutes. On pouring into water, 3 : 5-dinitro-*p*-tolyl-*n*-butylnitroamine was obtained as a pale yellow solid. It was purified by extracting it three times with hot water and recrystallising from aqueous alcohol (80 per cent.). It was also obtained readily from 3 : 5-dinitro-*p*-tolyl-*n*-butylnitrosoamine by dissolving the latter in nitric acid (D 1·5) and allowing the solution to remain. The nitroamine crystallised in almost colourless needles. After filtering through glass wool and washing with water, it was obtained pure by one crystallisation from methyl alcohol:

0·0694 gave 0·1130 CO_2 and 0·0280 H_2O. C = 44·40; H = 4·48.
0·0706 „ 11·8 c.c. N_2 at 25·5° and 746·5 mm. N = 18·78.
$C_{11}H_{14}O_6N_4$ requires C = 44·28; H = 4·73; N = 18·79 per cent.

3 : 5-*Dinitro*-p-*tolyl*-n-*butylnitroamine* is readily soluble in most of the common organic solvents, sparingly so in light petroleum,

and almost insoluble in water. On gently warming with sulphuric acid and phenol, as in Liebermann's reaction, a green coloration is obtained which changes, on dilution, through a succession of colours to reddish-brown. This coloration reverts to green on rendering alkaline. An alcoholic solution of potassium hydroxide produces a red coloration, which becomes much darker on warming. A dilute solution of potassium cyanide when added to a solution of the nitroamine gives no coloration, but on warming the solution becomes brown.

2:3:5-*Trinitro*-p-*tolyl*-n-*butylnitroamine*.

To 2-nitro-*n*-butyl-*p*-toluidine (4 grams), 45 grams of nitric acid (D = 1·5) were added slowly so that the temperature of the mixture was 30—60°. The reaction was completed by heating at 80—90° for a short time. On pouring the mixture on ice, the compound separated in a crystalline form, and on recrystallisation from aqueous alcohol it was obtained in white needles melting at 87—88°:

0·0754 gave 13·4 c.c. N_2 at 22·5° and 757·3 mm. N = 20·46.
$C_{11}H_{13}O_8N_5$ requires N = 20·41 per cent.

It is readily soluble in benzene or chloroform, moderately so in cold methyl alcohol, but readily so in the boiling solvent. By using less nitric acid, a product was obtained melting at 80° after several crystallisations from aqueous alcohol. On crystallisation from nitric acid, the melting point was raised to 87—88°, and a mixture of this compound with 2:3:5-trinitro-*p*-tolyl-*n*-butylnitroamine also melted at 87—88°. The original compound before crystallisation from nitric acid was therefore the nitrosoamine.

2 : 3 : 5-*Trinitro*-p-*tolyl*-n-*butylnitrosoamine*.—Finely powdered 2-nitro-*n*-butyl-*p*-toluidine sulphate (2 grams) was gradually added to a mixture of nitric acid (D 1·4 : 14 grams) and concentrated sulphuric acid (33 grams), and the mixture kept at 30—35° for two hours. The reaction was completed by heating on the water-bath for five minutes. On pouring the mixture on ice, a viscid, sulphur-yellow product was obtained after washing with cold water, and after several crystallisations from aqueous alcohol it was obtained in very pale yellow crystals melting at 80·5°:

0·0734 gave 14·1 c.c. N_2 at 23° and 743·3 mm. N = 21·67.
$C_{11}H_{13}O_7N_5$ requires N = 21·41 per cent.

*Nitration of Di-*n*-butyl-*p*-toluidine.*

Di-*n*-butyl-*p*-toluidine was nitrated under conditions similar to those used in the nitration of mono-*n*-butyl-*p*-toluidine, namely, using an excess of nitric acid in glacial acetic acid, and by nitration in the presence of an excess of sulphuric acid.

Nitration by means of fuming nitric acid in glacial acetic acid proceeded vigorously, the reaction being controlled, when necessary, by the addition of a further quantity of acetic acid and by cooling. The product was isolated in the usual way, and, after recrystallisation from absolute methyl alcohol, melted at 57°. Analysis (Found: N = 19·85. Calc.: N = 19·86 per cent.) showed that the compound was 3:5-dinitro-*p*-tolyl-*n*-butylnitrosoamine, and a mixture of this compound obtained from 3:5-dinitro-*n*-butyl-*p*-toluidine by the action of nitrous acid with the above product also melted at 57°. By vigorous nitration, one of the alkyl groups of dibutyl-*p*-toluidine is therefore removed. It was observed that after the nitration mixture had been poured on ice and then allowed to remain for a short time, there was an odour resembling that of propionic acid or one of the lower members of the fatty acid series.

Di-*n*-butyl-*p*-toluidine (1 mol.) dissolved in a large excess of concentrated sulphuric acid was nitrated by the addition of the calculated amount of nitric acid (1 mol.) also dissolved in concentrated sulphuric acid. It gave 2-nitro-di-*n*-butyl-*p*-toluidine, which was isolated in the usual manner after pouring the mixture on ice and rendering alkaline:

0·0836 gave 8·16 c.c. N_2 at 28° and 742·3 mm. N = 10·81.
$C_{15}H_{24}O_2N_2$ requires N = 10·60 per cent.

2-*Nitrodi-*n*-butyl-*p*-toluidine*, which was obtained as a red oil, is miscible with most of the common organic solvents. It forms salts which are hydrolysed by water, and is characterised by its *hydrochloride*, which is obtained as a white precipitate on adding an excess of concentrated hydrochloric acid to an aqueous suspension of the base:

0·1247 gave 0·0610 AgCl. Cl = 12·11.
$C_{15}H_{24}O_2N_2,HCl$ requires Cl = 11·79 per cent.

Titration with Titanous Chloride.—0·0099 required 8·2 c.c. $TiCl_3$ (1 c.c. = 0·001351 gram Fe). Calculated for $C_{15}H_{24}O_2N_2,HCl$ = 100·4 per cent.

In order to determine the position of the nitro-group, the substance was further nitrated. To a solution of it (1 mol.) in ten times its weight of glacial acetic acid, forty times its weight of

nitric acid (D 1·5) was added slowly. After the mixture had remained for two or three hours, it was heated on the water-bath until the evolution of nitrous fumes ceased. On pouring into water, a pale yellow oil was obtained, solidifying to a brown mass, which on crystallisation from alcohol gave almost white needles melting at 80° (Found: N = 21·3), and a mixture of these with the product obtained by nitrating 2-nitro-*n*-butyl-*p*-toluidine melted at the same temperature. It was therefore 2:3:5-trinitro-*p*-tolyl-*n*-butylnitrosoamine (Calc.: N = 21·41 per cent.). If the nitro-group in the original compound were in position 3, then a dinitromonobutyl-*p*-tolyl derivative might be expected. On the other hand, 2-nitrodi-*n*-butyl-*p*-toluidine would be expected by vigorous nitration to lose a butyl group and yield the same product as 2-nitromono-*n*-butyl-*p*-toluidine. This was actually found to be the case. The evidence, therefore, is in favour of the view that the nitro-group in the mononitro-compound obtained by nitrating di-*n*-butyl-*p*-toluidine in sulphuric acid is in the ortho-position with respect to the methyl group.

[*Received, November 7th*, 1918.]

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1918.

INDEX OF SUBJECTS.

TRANSACTIONS. 1918.

Single organic compounds of known empirical formula will be found in the Formula Index, p. 1004.

FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

C_2 Group.

C_3 Group.

C_4 Group.

C_5 Group.

C_6 Group.

C_7 Group.

C_{11} Group.

C_{12} Group.

C_{13} Group.

C_{14} Group.

C_{15} Group.

C_{16} Group.

C_{17} Group.

C_{18} Group.

C_{19} Group.

C_{20} Group.

C_{25} Group.

C_{26} Group.

C_{27} Group.

C_{28} Group.

C_{29} Group.

C_{30} Group.

C_{32} Group.

ERRATA.

VOL. CXI. (TRANS., 1917).

Page	Line	
243	15*	*for* "water" *read* "oxygen."
774	15*	,, "sodium hypochlorite" *read* "potassium permanganate."

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Page	Line	
31	19	,, "$C_{16}H_{15}O_2N_2$" *read* "$C_{16}H_{14}O_2N_2$."
100	3*	,, "4-*di*-n-*butylaminoazobenzene*-4′-*sulphonic acid*" read "4-p-*sulphobenzeneazodi*-n-*butylaniline*."
100	1	,, "4-n-*butylaminoazobenzene*-4′-*sulphonic acid*" read "4-p-*sulphobenzeneazo*-n-*butylaniline*."
122	16*	,, "$Ce_2(C_{18}H_{31}O_2,O)_3$" *read* "$Ce(C_{18}H_{31}O_2,O_2)_3$."
123	4	,, "(Average temperature)" *read* "(Room temperature)."
540	4	,, "+ 50·6°" *read* "− 50·6°."
774	6	,, "$C_{20}H_{15}O_7$" *read* "$C_{20}H_{14}O_7$."

* From bottom.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, January 17th, 1918, at 8 p.m., Professor W. J. Pope, C.B.E., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Charles Bradshaw	June 21st, 1888	July 3rd, 1917
Reginald C. Woodcock..........................	Dec. 7th, 1871.	Jan. 5th, 1918

Messrs. H. J. Cunningham, W. A. Dickie, F. Bridge, and O. A. Le Beau were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of:

Ernest Atkinson, 5, Bank Road, Workington.
Albert Leslie Bloomfield, B.A., Rose Cottage, Epping New Road, Buckhurst Hill.
Joseph William Christelow, B.Sc., Highcliff View, Guisborough.
Thomas Gifford Elliot, Hillcote, Park Edge, Hathersage, Sheffield.
Frederick Page Evans, B.Sc., 8, Vicarage Road, Frindsbury, Rochester.
Cecil Stevenson Garnett, 12, Cross Street, Chesterfield.
Frederick Horace Garner, M.Sc., 172, St. Paul's Road, Balsall Heath, Birmingham.
Francis Clint Guthrie, B.A., The Roscote, Heswall, Cheshire.
Alan Haythornthwaite, B.Sc., 79, Clapham Common, West Side, S.W.4.
William Earl Hughes, B.A., 6, Coleherne Terrace, Earl's Court, S.W.5.
Herbert Spencer Kipling, West End House, Victoria Road, Stechford, Birmingham.
Francis Charles Lewis, B.Sc., Nwch-y-don, Elkington Road, Burry Port, Carm.
William Jackson Lund, M.Sc., "Penryn," Temple Road, Stowmarket.

Archibald Bruce Macallum, 243, College Street, Toronto.
Alfred Bertram Mann, 85, Laburnum Avenue, Garden Village, Hull.
Tudor Wiliams Price, B.A., M.Sc., "Gowanlea," Caledonia Road, Saltcoats.
Robert Ray, B.Sc., Eastriggs, Dumfriesshire.
Ferdinand Roques, 36, Rue Ste. Croix de la Bretonnerie, Paris.
Alfred Ulrich Max Schlaepfer, 12 Arlington Gardens, Chiswick.
William Leonard Scotcher, Eastriggs, Dumfriesshire.
Harold Pethick Shilston, 49, Radnor Drive, Wallasey, Cheshire.
George Taylor, 32, Sotheby Road, Highbury, N.5.
John Trotter, M.A., D.Sc., c/o Mactaggart, 12, Meadow Place, Edinburgh.
Arthur William Willis, 30, Manor Road, Stechford, Birmingham.
Charles Edmund Wood, M.Sc., 83, Kingswood Road, Moseley, Birmingham.

ORDINARY SCIENTIFIC MEETING.

The next Ordinary Scientific Meeting will be held on Thursday, February 7th, 1918, at 8 p.m.

LECTURE.

At the Ordinary Scientific Meeting on February 21st, at 8 p.m., Professor the Hon. R. J. Strutt, M.A., Sc.D., F.R.S., will deliver a Lecture entitled "Recent Studies on Active Nitrogen." A ballot for the election of Fellows will also be held on this day.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY MEETING ON THURSDAY, FEBRUARY 21st, 1918.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Atkinson, Ernest, A.M.I.E., F.R.M.S., M.I. & S.Inst., 5, Bank Road, Workington. Engineer and Metallurgist. Educated in Analytical Chemistry under Mr. Geo. Valentine, Chief Research Chemist, Workington Iron and Steel Co., Ltd.; Iron and steel expert for the Tasmanian Government, Highland Railway Co., etc. (*Signed by*) G. S. Blake, C. H. Ridsdale, Weldon Hanson, *N. D. Ridsdale, J. E. Stead, H. Frankland, Ernest W. Jackson.*

Barber, Charles Frederick Lee, 12, Queen's Terrace, Otley, Yorks. Leather Works Manager. Diploma in Leather Manufacture and Leather Trades Chemistry, Leeds University; two years' experience as Leather Works Chemist, later appointed Manager; co-author of two papers published in the Journal of the Society of Leather Trades' Chemists for October, 1917. (*Signed by*) Henry R. Procter, J. B. Cohen, H. M. Dawson, G. H. J. Adlam, Frank N. Harrap.

Bloomfield, Albert Leslie, Rose Cottage, Epping New Road, Buckhurst Hill, Essex. Chemist. Graduate of Oxford University, 2nd Class Honours Chemistry; (late Open Scholar of New College, Oxford); Chemist to Messrs. A. Boake, Roberts and Co., Ltd., Carpenter's Road, Stratford, E. (*Signed by*) J. E. Marsh, N. V. Sidgwick, Thos. H. Durrans, Alexander Hynd, G. R. Clemo.

Boothman, John, Oak Villas, Whitley Bridge, S.O., Yorks. Chemist and Works Manager. Studied Chemistry under the late J. Croysdale, Esq., F.C.S.; also had a course under J. S. Remington, Esq., Aynsome, Lancashire; have had twenty years' experience of laboratory work; at present and for the last fifteen years have been in charge of the sulphuric acid and fertiliser plants at Messrs. J. Croysdale and Sons, Ltd., Whitley Bridge. (*Signed by*) John Stewart Remington, C. Smith, Fred Taylor, J. H. Garner, *Arthur S. Robinson.*

Christelow, Joseph William, Highcliff View, Guisborough, Yorks. Captain, Royal Engineers, formerly Research Student in Chemistry at University College, Reading. B.Sc. London, 2nd Class Honours in Chemistry; one year's research experience as above; Associate of the Institute of Chemistry of Great Britain and Ireland. (*Signed by*) Henry Bassett, jun., Arthur E. Everest, J. W. Dodgson, J. P. Batey, *J. Archyll Jones.*

Coakill, Edgar Alfred, 206, Green Street, Brimsdown, Middlesex. Analytical Chemist. Scholarship holder at Finsbury Technical College; passed three-year course in organic and inorganic; awarded certificate on leaving; assistant chemist in laboratories of three Portland cement works, analytical work covering cement, clay, sand, fuels, general stores, etc.; shift (works) chemist at lead works; charge of operations in manufacture of lead compounds, *e.g.* carbonate, oxide, silicate, nitrate, thiosulphate, etc.; now at Royal Small Arms Factory, analysis of iron and steel, also copper, zinc, lead, tin and nickel alloys, general stores, etc. (*Signed by*) John D. Speed, Arthur J. Hale, G. T. Morgan, *Percy Edgerton, Thomas A. Henry.*

Cooper, Ransome Wallace, Chiltern Place, Beaconsfield. Analytical Chemist and Paint Manufacturer. Honours Prizeman and Medallist, City and Guilds Examination, "Technology of Painters' Oils, Colours, and Varnishes"; Chemistry: Science and Art Department, Honours, Part I.; Inorganic: Prac. and Theo.; Organic: Prac. and Theo. Advanced; Lecturer on leadless paints. (*Signed by*) F. G. Adair Roberts, A. Boake, Isaac S. Scarf, A. J. de Hailes, W. G. Aston, *R. C. Menzies.*

Crowdy, Thomas, A.M.S.E., A.M.C.I., M.J.I.E., M.I.C.T., Member Soc. Chemical Ind. Gas Assoc. Gas Engineer and Chemist, 13, Clifton Road, Devizes Road, Salisbury. Assistant Controller, Trench Warfare Depôt. Chemist and Engineer. Articled to N. H. Humphrys, Esq., F.C.S., etc., Salisbury, to learn profession of Gas Engineer and Chemist; after serving five years was appointed Works Chemist to the Salisbury Gas Co., from 1903 to 1916. In February, 1916, I was appointed by the Ministry of Munitions to fill the post of Analytical Chemist for the T.W. Department. I specialised in poison gas and the destruction of these gases. I did much research work for Mr. Humphrys in connection with oil-refractory materials: Tar—and products, china clay, T.N.T., petrol in gas, and oil gas, etc., etc. City and Guilds of London Institute Technologist certificates, viz., (1st Class Final Honours), (2—1st Class), and (1—2nd Class). (*Signed by*) N. H. Humphrys, Thos. Tyrer, J. P. Longstaff, *J. H. Canning, Philip G. G. Moon, R. Lessing.*

Drew, Harry Dugald Keith, 94, Cambridge Street, Warwick Square,

S.W. Civil Servant, at present serving with Royal Naval Air Service. B.Sc. (London); 1st Dn. in Chemistry, Physics, and Applied Mathematics; Student in Chemistry of Birkbeck College, London; part author of papers in the Journal of the Society, Trans. **107** (1915), 26; **107** (1915), 628; **109** (1916), 1091. (*Signed by*) George Senter, F. Barrow, G. H. Martin, Geoffrey Martin, G. W. Clough.

EASTICK, JOHN CLARE NEWLANDS, 137 Upper Clapton Road, London, E.5. Passed through three years' Chemical Course at Finsbury Technical College; studied under the late Mr. B. E. R. Newlands, F.I.C., and the late Mr. J. J. Eastick, F.I.C., A.R.S.M. Partner in J. J. Eastick and Sons, Consulting and Analytical Chemists; Captain in charge of Irish Command Anti-Gas School. (*Signed by*) Chas. E. Eastick, Fred C. Eastick, L. J. de Whalley, *Charles A. Keane*, *Ern. W. Harvey*.

EDWARDS, FREDERICK WILLIAM, 283, Friern Road, Dulwich, S.E.22. Analytical Chemist. Studied Chemistry and Physics in the laboratories at Charing Cross Hospital Medical School, 1904–1907. Assistant to P. A. Ellis Richards, Esq., F.I.C.; Public Analyst for the City of Westminster and the Borough of Hammersmith, 1907 to present time, being engaged in the examination of food, drugs, water, etc., and in toxicological and pathological analyses. (*Signed by*) P. A. Ellis Richards, Cecil H. Cribb, E. Richards Bolton, Hugh C. H. Candy, Cecil Revis.

ELLIOT, THOS. GIFFORD, Hillcote, Park Edge, Hathersage,, *viâ* Sheffield. Metallurgical Chemist. Fellow of Institute of Chemistry; Chief Chemist and Metallographist of Hadfield's, Ltd., Hecla Works, Sheffield. Author of paper on "The Volumetric Estimation of Sulphur in Iron and Steel," given to Iron and Steel Institute, May, 1911. (*Signed by*) R. A. Hadfield, John Evans, Jas. T. Stevenson, W. P. Wynne, Frederick J. Merrils.

EMERSON, FREDERICK WILLIAM, 179, Burton Road, West Didsbury, Manchester. Research Chemist in Intermediates and Dyestuffs. After a three years' course in Bleaching, Dyeing, and Printing, I became an Associate of the School of Technology, Manchester. From there I took up a position as Research Chemist at Messrs. Claus and Co., Ltd., Aniline Dye Manufacturers, with whom I have now been for two and a half years. (*Signed by*) Robt. D. Abell, Frank Brinsley, F. W. Atack, W. D. Rogers, Raymond E. Crowther.

EVANS, FREDERICK PAGE, 8, Vicarage Road, Frindsbury, Rochester, Kent. Chemist with Messrs. Curtis's and Harvey, Ltd. Student at University College, London, for three years, 1911–14. Graduated in 1914. B.Sc. Honours in Chemistry (2nd Class). Since then two years at the Explosive Works of Messrs. Curtis's and Harvey, Ltd., as Chemist in Laboratories and on Guncotton Plant. (*Signed by*) J. N. Collie, F. G. Donnan, W. B. Tuck, Samuel Smiles, Geo. W. MacDonald.

FIELDING, CHARLES HENRY, Minerva, College Road, Cork. Pharmaceutical Chemist. Also studied General and (as per occupation) Pharmaceutical Chemistry (Practical and Theoretical), under the personal teaching of Prof. J. Taylor, M.Sc., at the Crawford Technical College, Cork, from the year 1905 to 1912, as well as a course of instruction at the Westminster College of Pharmacy, London, under Mr. G. S. V. Wills. (*Signed by*) Michael A. Fielding, Patrick J. Fielding, Patk. T. O'Sullivan, *Daniel O'Mahony*, *Thos. Farrington*.

FLEMING, ROBERT, B.A. (Sen. Mod.) Dublin, 2, Wabour El Moyah, Cairo, Egypt. Lecturer in Chemistry under the Egyptian Government at the High Training College, Cairo. Senior Moderatorship in Experimental Science

(Chemistry and Physics) with Gold Medal, Dublin University; Associateship in Applied Chemistry, Royal College of Science for Ireland; Science Teacher, now Lecturer in Chemistry, High Training College, Cairo. (*Signed by*) Sydney Young, Emil. A. Werner, A. G. G. Leonard, *W. E. Adeney, Richard J. Moss.*

FRAZER, THOMAS, The Grammar School, Cirencester, Glos. Headmaster of the Cirencester Grammar School. B.A. Trinity College, Dublin; B.A. Royal University of Ireland. (*Signed by*) Sydney Young, Emil. A. Werner, J. B. Coleman, J. C. Crocker, F. H. Lowe.

GARNER, FREDERIC HORACE, 172, St. Paul's Road, Balsall Heath, Birmingham. Research Chemist. B.Sc., 1st Class Hons. in Chemistry, 1914; M.Sc., 1915, obtained at the University of Birmingham; engaged on Chemical Research with Professor P. F. Frankland, F.R.S., from 1913–1917. (*Signed by*) Percy F. Frankland, Adrian J. Brown, Frederick Challenger, W. E. Garner, Geo. King, *Oscar L. Brady.*

GARNETT, CECIL STEVENSON, 12, Cross Street, Chesterfield. Analyst. Associate in Metallurgy, Sheffield University. Desire to take the Journal of the Society, and to have the use of the Library. (*Signed by*) W. P. Wynne, John Evans, W. E. S. Turner, *L. T. O'Shea, Jas. T. Stevenson.*

GELDARD, JULIUS, 610, St Helens Road, Bolton. Works Chemist with Messrs. Ed. Bennis and Co., Ltd., Little Hulton, Bolton. Three years Leeds University; one year's research with Professor A. G. Perkin; five years Works Chemist, G. Armitage, Ltd., Bradford Dyers' Association; twelve years Ed. Bennis and Co., Ltd., Bolton, Coal, Iron, and Steel Analysis. (*Signed by*) Walter Leach, Fred Ferrand, Walter M. Gardner, A. G. Perkin, J. B. Cohen.

GRANT, WILLIAM FRANK, The Normal Training College, Bloemfontein, O.F.S. Lecturer in Science and Mathematics, Normal College, Bloemfontein. B.Sc. (Chemistry), London, 1910; Hons. student in Chemistry under Professor K. J. P. Orton, at the Univ. College of N. Wales, Bangor (1910); Senior Chemistry Master, S.A. College High School, Cape Town, 1912–1917. At present Lecturer in Science and Mathematics to students in training at The Normal Training College, Bloemfontein, O.F.S. Author of the chemistry portion of "Physical Science for Matriculation" (Juta and Co., Cape Town), and of "The Teaching of Chemical Theory without the aid of Dalton's Atomic Theory and Avogadro's Hypothesis." The latter is at present in the press. (*Signed by*) F. W. Storey, A. Peacock, B. M. Narbeth, Andrew Young, *J. S. Jamieson.*

GRIST, WILLIAM ROBINSON, Finsbury Technical College, Leonard Street, E.C.2. Research Chemist. Teacher of Chemistry, Municipal Secondary School, Scarborough, 1905–1917; Research Scholar, Chemical Department, Finsbury Technical College, 1917. (*Signed by*) G. T. Morgan, A. W. H. Upton, A. J. Hale, Percy Edgerton, *J. A. Goodson.*

GUTHRIE, FRANCIS CLINT, The Roscote, Heswall, Cheshire. Analytical Chemist. B.A. Cantab, Natural Science Tripos, Part I. Chemistry, Physics, Geology, 1910; A.I.C., 1914. (*Signed by*) W. C. McC. Lewis, E. C. C. Baly, Alfred Holt, Herbert H. Froysell, Robert Robinson.

HANSON, JOSEPH ELI, Quarry House, Ossett Lane, Earlsheaton, Dewsbury. College-trained Certificated Teacher. Certificated College-trained Teacher; Matriculations London and Leeds; Associate of Royal Sanitary Institute (A.R.S.I.); Member of Institute of Hygiene (M.I.H.); Dispensing (Chemistry), (Soc. of Apothecaries); Fellow of the Society of Science (F.S.Sc.); Science in L.C.P.; Special College Certificate in Optional Chemistry

(Carmarthen College). (*Signed by*) R. Gawler, A. E. Holmes, R. S. Cahill, C. E. Womersley, *H. J. Taylor*.

HARDIKER, ERNEST, 3, Park Street, Bolton. Acting Chief Assistant to Mr. W. J. Smith, B.Sc., Gas Engineer and Manager, Bolton. Engaged in the supervision of the manufacture and purification of coal gas, and plant producing concentrated ammonia, sulphate of ammonia, crude benzol, etc., and also control of analytical work connected therewith. Studied Chemistry at Manchester School of Technology. Desire Fellowship to keep in touch with Modern Research through Society's publications. (*Signed by*) Robt. P. Douglas, C. A. Fogg, F. S. Sinnatt, R. L. Taylor, *John Allan, E. L. Rhead*.

HAYTHORNTHWAITE, ALAN, 79, Clapham Common, West Side, S.W.4. Chemist. Bachelor of Science (1st Class Hons. Chemistry), London; Associate of the Royal College of Science, London; Associate of the Institute of Chemistry. (*Signed by*) Charles Gilling, Arthur J. Ewins, R. Blenkinsop, A. H. M. Muter, J. W. Epps.

HITCHCOCK, THOMAS JOHN, 28, Albany Road, Manor Park, London, E.12. Research Technologist. Chief Chemist to the Sugar and Malt Products Co., London, for the last eight years. Chemist to A. Boake, Roberts and Co., Ltd., London, 1908–09; studied at East London College, and also under London Public Analyst; have been engaged for some years past in research in sugar and allied products. (*Signed by*) A. Boake, F. G. Adair Roberts, T. May Smith, Thos. H. Durrans, *Alex. K. Miller*.

HOUSLEY, HAROLD, Huntsville, St. Andrew's Road, Huddersfield, Yorks. Works and Research Chemist. B.Sc. Hons. Chem., 2nd Class, 1914, Manchester University; M.Sc., 1915, Manchester University; Research Assistant to Professor H. B. Dixon, F.R.S.; later Works Chemist to Messrs. British Dyes, Ltd., Huddersfield. (*Signed by*) H. B. Dixon, Arthur Lapworth, F. P. Burt, Norman Smith, J. E. Myers.

HOWELL, OWEN RHYS, Darley House, Venner Road, Sydenham, S.E.26. Research Chemist with South Metropolitan Gas Company. B.Sc. with 1st Class Honours in Chemistry (Univ. Wales, Aberystwyth); University Student in Chemistry; Scholar of Royal Exhibition of 1851. Contributions with Professor Findlay: "Solubility of Nitrous Oxide in Colloids," *J.C.S.*, 1914, 291; "Solubility of Carbon Dioxide in Starch," *J.C.S.*, 1915, 282; another paper in preparation for publication. Technical Research Work under E. V. Evans, Esq., F.I.C., Chief Chemist, South Metropolitan Gas Company since April, 1916. (*Signed by*) Alex. Findlay, T. Campbell James, E. V. Evans, *Kennedy J. P. Orton, Claude M. Thompson*.

HUGHES, WILLIAM EARL, 6, Coleherne Terrace, Earl's Court, London, S.W.5. Lieut., R.F.C., and 3rd Leicester Regt. Nat. Sci. Tripos; late Examiner in Electro-metallurgy to the City and Guilds of London Institute; head chemist (for several years) to W. Canning and Co., London and Birmingham; Research Electro-metallurgist at the Royal Aircraft Factory, S. Farnborough, etc., and barrister-at-law (Middle Temple). (*Signed by*) John O. Hughes, Gilbert Palmer, Bertram Campbell, *A. Chaston Chapman, Fred. T. Harry*.

KIPLING, HERBERT SPENCER, West End House, Victoria Road, Stechford, Birmingham. Metallurgical Chemist. Pupil under Messrs. Pattinson and Stead, Middlesbrough, 18/6/00 to 31/7/04; metallurgical chemist, W. Beardmore and Co., Glasgow, 1/8/04 to 11/1/08 (from September, 1904, onwards in charge of research laboratory of Armour Dept.); chief assistant chemist, Weardale Steel, Coal, and Coke Co., 14/1/88 to 31/12/09; chemist, Lysaghts Ore-field, 3/1/10 to 1/4/10; assistant chemist, Messrs. Pattinson and Stead, Middlesbrough, 4/4/10 to 19/5/10; chief chemist and metal-

lurgist, Wolseley Motors, Ltd., since 23/5/10; member of Iron and Steel Institute; member of Foundrymen's Association. (*Signed by*) J. E. Stead, H. Frankland, Ernest W. Jackson, *C. H. Ridsdale*, *N. D. Ridsdale*.

KIRKWOOD, THOMAS WILLIAMSON, "Brooklyn," Guildford Road, Farnborough, Hants. B.Sc. (Dunelm), Armstrong College, Newcastle-on-Tyne (1911–14); Chemistry Master at Hipperholme Grammar School, near Halifax, Yorkshire (1914–1915); Assistant Chemist at Royal Aircraft Factory (Jan. 3, 1916—to date). (*Signed by*) P. Phillips Bedson, J. A. Smythe, J. O. Hughes, A. U. Newton, Bertram Campbell.

LAIWALA, KUMUDCHANDRA GHELABHAI, Balaji Road, Surat. Post-graduate Student. M.A., B.Sc. (Bombay University); Research on the "Hydrolysis of Oils by Lipase," under publication (Journal of the Indian Institute of Science). (*Signed by*) W. H. Simmons, J. Wilson, J. L. White, J. P. Longstaff, *Edward L. Joseph*.

LAWRENCE, HAROLD, Ridge View, 81, Foxley Lane, Purley, Surrey. Manufacturing Chemist. A keen interest in the advancement of applied science, particularly in the manufacture of synthetic compounds and coal-tar derivatives. (*Signed by*) G. F. Morrell, Walt. R. Pratt, G. H. Pierson, F. W. Crossley-Holland, *C. E. Corfield*.

LEWIS, FRANCIS CHARLES, Uwch-y-don, Elkington Road, Burry Port, Carm. Superintendent of T.N.T. Department, H.M. Factory. B.Sc., Wales, with 1st Class Honours in Chemistry; employed by Messrs. Nobel's Explosives Co., Ltd., since July, 1915; from July, 1915, to Jan., 1916, as a shift chemist, and since Jan., 1916, as superintendent of T.N.T. Dept. (*Signed by*) Claude M. Thompson, E. P. Perman, Robt. D. Abell, Ernest Vanstone, E. J. Amies, Edgar Lewis.

LOWNDES, ARNOLD BRADLEY, 78, Wellesley Road, Ilford, Essex. Petty Officer, Chemist, R.N.A.S. Five years' practical and theoretical chemical study; Inter. B.Sc. (Internal) Birmingham; further academic work interrupted by war; Petty Officer Chemist, Royal Naval Air Service, Chemical Experimental Station; two years' actual contact with large chemical plant. (*Signed by*) T. Slater Price, J. E. Coates, Sidney A. Brazier, Maurice E. Probert, F. C. Laxton, Frederick Challenger, *Thos. Tyrer*.

LUND, WILLIAM JACKSON, "Penryn," Temple Road, Stowmarket, Suffolk. Works Chemist. B.Sc. Tech. degree on completion of three years' course at the Manchester School of Technology; M.Sc.Tech. on presentation of thesis entitled, "The Function of Water in the Combustion of Carbon Monoxide"; Chemist to the Manchester Air Pollution Board (1914), The New Explosives Co., Ltd. (1915). (*Signed by*) H. F. Coward, Edmund Knecht, Stanley J. Peachey, E. L. Rhead, G. G. Quinn.

MACALLUM, ARCHIBALD BRUCE, 243, College Street, Toronto, Ont. Research Chemist. Educated at the Universities of Toronto and Munich; author of many papers on biochemical subjects; now engaged in research bearing on the preparation of synthetic drugs. (*Signed by*) Arthur Harden, George Barger, J. C. Drummond, R. H. A. Plimmer, Robert Robison.

MANN, ALFRED BERTRAM, 85, Laburnum Avenue, Garden Village, Hull. Works Chemist. Theoretical and Practical Courses in Inorganic, Organic, and Applied Chemistry; Sound, Light, and Heat, Magnetism, and Electricity, etc., the Hull Technical College; Senior Oxford Local Exam.; prize winner and Bronze Medal in Oils, Fats, and Waxes Exam. (London City and Guilds); prize winner and Bronze Medal in Painters' Colours, Oils, and Varnishes; seven years Assistant Chemist for Messrs. Blundell, Spence and Co., Ltd., Paint and Colour Manufacturers; served with the Chem. Corps,

Royal Engineers, May to September, 1916, when I was recalled for appointment as a Chemist at H.M. Factory. (*Signed by*) R. Ferguson, Thos. A. Nightscales, T. Luxton, Wm. Geary, *Harry Thompson*.

MENDOZA, ELIAS, 55, Manor Road, London, N.16. Chemist. Employed at Royal Aircraft Factory. Associate of the Institute of Chemistry. Have carried out investigation work on castor oil and on lubricating oils used in aeroplane engines. (*Signed by*) J. O. Hughes, Gilbert Palmer, Bertram Campbell, A. W. H. Upton, Arthur J. Hale.

MORGAN, JOHN RICHARD, 8, Heathcote Close, Ash Common, Surrey. Assistant Chemist, Royal Aircraft Factory. B.Sc. (Wales); Honours in Chemistry (1915); and have been engaged on chemical work in connection with Cellulose Acetate, Dopes, Varnishes, etc., at the R.A.F. for the last two and a half years. (*Signed by*) Kennedy J. P. Orton, John O. Hughes, Gilbert Palmer, Bertram Campbell, Arthur U. Newton.

MUNRO, ARTHUR MACDONALD, Auckland, New Zealand. At present residing at 44 Rossett Road, Blundellsands, near Liverpool. Analytical and Technical Chemist, H.M. High Explosive Factory. M.A. Oxon., St. John's College; Hons. in Chemistry, 1911; Associate of the Institute of Chemistry; Research Student and Graduate of the University of New Zealand, 1913; Instructor and Lecturer in Chemistry, Physics, Physiology, Botany, and Hygiene at the Wellington Technical College, N.Z., 1914–1915; Science Master at King's College, Auckland, N.Z., 1915–1916; selected and sent by the Australian Government in 1917 to England to join the Ministry of Munitions. (*Signed by*) T. S. Moore, F. D. Chattaway, N. V. Sidgwick, B. Lambert, J. E. Marsh.

NAIR, THEKETH KUMARAN, B.A. (Madras), B.Sc. (Birmingham), Jamalpur, E.I. Railway. Chemist and Metallurgist to the East Indian Railway Company. Graduate at the Madras University; Graduate at the Birmingham University; conducted research work in the Birmingham University, and published the same in the *Journal of the Chemical Society* (*vide* page 1534 of 1913. (*Signed by*) C. T. Foreman, Thomas Turner, Percy F. Frankland, *Harry Silvester, Frederick Challenger, A. Parker*.

ODDY, ROBERT ATKINSON, The Laboratory, Abbey Street, Toad Lane, Rochdale. Analytical Chemist. I am twenty-nine years old, and have been engaged for the last eleven years as Assistant to Robert W. Oddy, F.I.C., F.C.S., Analytical and Consulting Chemist. My work has consisted in the analysis of Foods, Waters, both for domestic and industrial supply (including the supervision of erection of Water-Softening Plants). My close contact with the cotton and woollen industry has caused me to study the numerous processes that raw cotton and wool undergo ere they become the finished article. I have had much work on the treatment of trade effluents covering some fifty plants installed. (*Signed by*) Robt. W. Oddy, Thos. Stenhouse, Wm. Marshall, W. H. Pennington, James H. Kershaw, Percy R. Strivens.

OXLEY, HORACE FINNINGLEY, c/o Messrs. Levinstein, Ltd., Blackley, Manchester. Research Chemist. Second Class Nat. Sciences Tripos, Camb., 1905 (Chemistry, Physics, Geology, Mineralogy); 1906 Course of Organic Chem. and Org. Research under Professor Pope, F.R.S., at Municipal School of Technology, Manchester; 1908–1914, Research in Catalytic Reactions and Manufacture of Hydrogen at Messrs. Jas. Crosfields and Sons, Ltd. (*Signed by*) W. J. S. Naunton, R. B. Forster, Thomas Callan, Charles E. Potter, G. Rigg, F. Robinson, Jas. A. Russell Henderson.

PEZZANI, HENRI MARC, Eastriggs, Dornock, Dumfriesshire. Sugar

Chemist. Specialised in Sugar Technology and Manufacture. Trained at the "Agronomical Station" of the Island of Mauritius. Had seven years' experience in sugar manufacture. Previous to the war, Chemist at the "La Mercy" Sugar Factory, Natal. Attached now for the period of the war to the staff of the Central Chemical Laboratory, H.M. Factory. (*Signed by*) David Hooper, Ernest W. Smith, Douglas Bowack, *H. R. Neech, E. Taberner, Percy J. Channon.*

PHILLIPS, DAVID JOHN PRICHARD, Pemberton Stores, Burry Port, Carmarthenshire. Superintendening Chemist, H.M. Factory. Assistant Science Master, County School, Brecon, 1914-1915; B.Sc. 2nd Class Honours Chemistry, University of Wales; Laboratory Chemist, April–September, 1915; Superintending Chemist, Propellants Department, since September, 1915, under Messrs. Nobel's, H.M. Factory. (*Signed by*) Claude M. Thompson, E. P. Perman, Robt. D. Abell, *Kennedy J. P. Orton, Alex. Findlay.*

PRICE, TUDOR WILLIAMS, "Gowanlea," Caledonia Road, Saltcoats, Ayrshire. Research Chemist. B.Sc. (Wales) with 1st Class Hons. in Chemistry, 1910; M.Sc. (Wales), 1912; B.A. (Cantab), 1914 (by research); 1851 Exhibitioner of University College, Cardiff, 1912–1914. Contributions: "Vapour-pressure of Concentrated Aqueous Solutions," *Trans. Faraday Soc.*, 1912, 8, 68 (with Dr. E. P. Perman); "Osmotic Pressure of Alcoholic Solutions," Part I., *J.C.S.*, 1915, 57, 188. Research Chemist with Messrs. Nobel's Explosives Co., Ltd., since August, 1914. (*Signed by*) William J. Pope, Claude M. Thompson, Wm. Rintoul, G. H. Beckett, Wm. Barbour.

RAY, ROBERT, B.Sc. (St. And.), B.Sc. (Cape), F.L.S., A.I.C., Eastriggs, Dumfriesshire. Senior Chemist in Charge Nitroglycerine Section. B.Sc. (St. And.), 1912. Graduated in the following subjects:—1st. B.Sc. Chemistry, Physics, Botany, Zoology, Mathematics. Final B.Sc.: Chemistry, Zoology, Geology, and Metallurgy. Other Grad. Classes taken: Anatomy, Physiology, Histology, Physiological Chemistry, Anthropology, etc. Carnegie Scholar, 1913. B.Sc. (Cape), 1915. F.L.S. (London), 1914. A.I.C. 1917. Assisted in the Research Laboratory (Zoological Dept.), Liverpool University, 1912–13. Assisted in the scientific activities of the Lancashire and Western Sea Fisheries, 1912–13. Appointed Lecturer in Biology in the South African College, Cape Town (Univ. of the Cape of Good Hope), 1913. Appointed Assistant Naturalist to the Government of S. Africa (Cape Province), 1914. Since war broke out I have worked on guncotton and nitroglycerine, also on the Quinan drying stoves at Messrs. Kynoch's. Now hold the position of Senior Chemist in Charge, Nitroglycerine Section, H.M. Factory. (*Signed by*) David Hooper, John Mitchley, H. R. Neech, Herbert E. Page, E. Taberner.

ROQUES, FERDINAND, 36, rue Ste. Croix de la Bretonnerie, Paris. Pharmacist of 1st Class of the Ecole Superieure de Paris; Manufacturing Chemist (manufacture in St. Ouen, near Paris). Sur la Cinchonicine cristallisée, Comptes rendus de l'Acad. des Sciences, t. cxx., page 1170; Récherches sur la Cinchonicine, thèse, Gauthiers, Villars et Fils, éditeurs, 1896; Golden Medal of the Société de Pharmacie de Paris, 1895-96; Remarques sur le bromure d'Ethyle du Codex, *J. de Pharmacie et de Chimie*, 1er Août, 1911; Regénération de la teinture d'Iode altérée, *J. de Pharmacie et de Chimie*, 16 Mars, 1914. Sur les sels de Cocaine employés quelquefois en thérapeutique, *Bulletin des Sciences pharmacologiques*, Mai, 1914. (*Signed by*) Thomas D. Morson, Alfred G. Howard, R. Blenkinsop, *Frank Moul, Charles Gilling, Arthur J. Ewins.*

Schlaepfer, Alfred Ulrich Max, 12, Arlington Gardens, Chiswick. Chief Chemist of the Chiswick Polish Co., Ltd. 1909, Immatriculation (Eidg. Naturität); 1909-1914, student at the Technical High School, Zurich; March, 1913, Diploma in Electrochemistry; March, 1914, Thesis: "Beiträge zur Kenntniss der hydrothermalen Silikate"; made Doctor of Technical Science (Doktor der technischen Wissenschaften E.T.H.); May-July, 1914, assistant of Prof. Dr. Forster at the Davy-Faraday Lab.; since May, 1915, with Chiswick Polish Co., Ltd. (*Signed by*) Percival John Fryer, James C. Philip, M. O. Forster, *H. B. Baker*, *S. Smiles*.

Scotcher, Wm. Leonard, Eastriggs, Dumfriesshire. Chemist in Charge, H.M. Factory, with practical training in nitrocellulose and acid manufacture. Ten years' laboratory experience at R.N. College, Greenwich, under late Professor V. B. Lewes; assistant to Professor J. S. S. Brame at R.N.C., Greenwich; also assistant instructor under Prof. Brame at practical fuel analysis and testing classes, Sir John Cass Inst., London; chemist for British Coalite Co. for research on tars and coals; private assistant in London to Prof. V. B. Lewes (late); Relief Gas Examiner for the City of London Corporation; practical experience, iron and steel examination, fuel analysis; member of Society of Chemical Industry; training in explosives manufacture, acid manufacture, etc., etc. (*Signed by*) John Mitchley, Herbert R. Neech, E. Taberner, David Hooper, Hubert E. Page.

Shilston, Harold Pethick, 49, Radnor Drive, Wallasey, Cheshire. Analytical Chemist. Student over three years in the laboratories of Messrs. Norman Tate and Co., Analysts, Hackens Hey, Liverpool, technical classes in about a dozen subjects being attended during that time; sixteen years chief assistant analyst to Messrs. Evans, Sons, Lescher, and Webb, Ltd., Wholesale Druggists, etc., Liverpool and London; three years in charge of testing staff of the same firm (twenty-two years' laboratory experience), which position I still hold; contributed to Evans' Analytical Notes for eight years. (*Signed by*) George Tate, Thomas J. Roberts, H. Humphreys Jones, *John Hanley*, *Ernest James Hoy*.

Tallantyre, Snow Blagburn, B.Sc., A.I.C., A.R.C.Sc., 14, Inglewood Road, West Hampstead, London, N.W.6. Technical Chemist. Analytical Chemist at Woolwich Arsenal (1912-1913); engaged in technical and analytical chemistry (three years, 1913-1916) at Messrs. Evans, Sons, Lescher, and Webb, Manufacturing Chemists, etc., Liverpool; now Research Chemist at H.M. Factory; Associate of the Institute of Chemistry of Great Britain and Ireland (1912); and B.Sc.(Lond.) 1st Hons. Chemistry (1911); Associate of the Royal College of Science, Imperial College of Science and Technology (1911). (*Signed by*) James C. Philip, Arthur A. Eldridge, M. O. Forster, Arthur Harden, G. T. Morgan, *A. T. King*.

Taylor, George, 32, Sotheby Road, Highbury, N.5. Analytical Chemist. Assistant to Dr. Bernard Dyer; Fellow of the Institute of Chemistry; Certificate of Finsbury Technical College. (*Signed by*) Bernard Dyer, J. F. H. Gilbard, Frank W. G. King, E. W. Voelcker, A. Chaston Chapman.

Taylor, John Cameron Clarke, Lieut. (General List), 2, Queensberry Terrace, Cummertrees, Annan, N.B. Industrial Research Chemist. Trained University of London. Chief Chemist to Arthur Smith, Manufacturing Chemist, Bramley, Leeds, 1910–13. Since then to 1915 investigated many technical processes in own Research Laboratory. From 1916 to present time, Chemist in the Department of Explosives Supply. (*Signed by*) E. Taberner, Douglas Bowack, Percy J. Channon, John Mitchley, Hubert E. Page, *Geoffrey Martin*, *Herbert R. Neech*, *David Hooper*.

THOMAS, HUGH ARWEL, 9, Church Circle, S. Farnborough, Hants. Analytical and Research Chemist, Royal Aircraft Factory. B.Sc. (Wales), 1914. From March, 1915, to present time engaged on Research work. I desire fellowship to extend my chemical knowledge and in order to use library. (*Signed by*) Kennedy J. P. Orton, J. O. Hughes, Gilbert Palmer, Bertram Campbell, *Alex Findlay*.

TIMMINS, ALBERT EDWARD, 81, Teasdale Road, Walney, Barrow-in-Furness. Metallurgical Chemist, Barrow Hematite Iron and Steel Company. Lecturer on Metallurgical and Engineering Chemistry, Theoretical and Practical, Technical Schools, Barrow-in-Furness. (*Signed by*) H. B. Weeks, A. R. Gower, E. L. Rhead, *F. S. Sinnatt, R. L. Taylor, S. J. Peachey, Jas. Grant*.

TROTTER, JOHN, c/o Mactaggart, 12, Meadow Place, Edinburgh. Agricultural Chemist and Agriculturist. Master of Arts, Bachelor of Science (Agric.), Bachelor of Science (Pure Science), and D.Sc. (Chemistry), of Edin. University; Fellow of the Highland and Agricultural Society; Works Chemist at Chance and Hunt's. (*Signed by*) D. Ivor James, T. A. Smith, R. W. L. Clarke, Wm. Wheatley, H. A. Scarborough, F. P. Dunn.

TWINE, GEORGE JOHNSTON, Sark Bridge, Gretna. Chemist. Engaged by Australian Government in 1916 to proceed to England as Chemist under the Ministry of Munitions. Technical training: "Diplomas" in Metallurgy, Metallurgical Chemistry and Assaying. Four years' course at Technical College, Mt. Morgan, Queensland, Australia. Works experience in following processes: Chlorination and Cyaniding Gold Ores, Smelting and Concentration of Copper Ores; several months' experience in each, M.M.G.M. Co., Ltd., Australia. Laboratory experience: Eight years in laboratory of the Mount Morgan Gold Mining Co., Australia, of which was spent: seven years as Assistant Chemist and Assayer; one year as Chemist in Charge of Laboratory. Additional works experience: Eleven months at H.M. Factory, as Chemist. (*Signed by*) David Hooper, Douglas Bowack, J. Bradshaw, J. C. Burnham, *Alfred Owen Jones*.

VLIES, LEONARD ELLERTON, "Belmont," Gowan Road, Manchester, S.W. Chemist and Director of Messrs. Claus and Co., Aniline Dye Manufacturers. Engaged during the last eighteen years in the introduction and manufacture of Dyestuffs in this country. Fellow of the Institute of Chemistry. (*Signed by*) Edmund Knecht, F. W. Atack, S. J. Peachey, Alex. K. Miller, J. C. Cain.

WAKEHAM, GLEN RAYMOND, Stanborough Park, Watford, Herts. Headmaster of Stanborough Park College. I have taught Elementary Chemistry for fifteen years; London B.Sc. (Hons. Chemistry); Analyst and Adviser to the International Health Association (manufacturers of diabetes biscuits, gluten, malt, nut, and other invalid foods). I wish to keep up to date in physiological and food chemistry, and in general chemistry for teaching purposes. (*Signed by*) W. F. Cooper, J. W. Shepherd, W. Briggs, *Harold G. Colman, J. A. Williamson*.

WARBURTON, GODFREY, Manager's House, Gas Works, Ponders End, Middlesex. Chief Chemist, Tottenham District Light, Heat, and Power Company. Three years pupil-assistant to late G. H. Hurst, F.C.S.; two years Chemist at Messrs. J. Brown and Co., Ltd., Manufacturing Chemists, Dewsbury, Yorks; one year special study in Chemistry and Physics at Victoria University, Manchester; six months Chemist and Assistant at Waterford Gas Works. For the past twelve years Chief Chemist to the Tottenham District Light, Heat, and Power Company. (*Signed by*) W. J. A. Butterfield, H. F. Hills, Harold G. Colman, *Patrick H. Kirkaldy, Edward Bevan*.

Wignall, Harry, 16 Roseneath Road, S.W.11. Research Chemist. M.Sc., Manchester University, 1915; A.I.C., 1917. Research Chemist since 1915 at the Admiralty Laboratories. (*Signed by*) Ch. Weizmann, Harold Davies, H. M. Spiers, E. G. Bainbridge, P. Haas.

Willis, Arthur William, 30, Manor Road, Stechford, Birmingham. Metallurgical Chemist. Five years' training in the laboratory of Messrs. Pattinson and Stead, Public analysts, Middlesbrough; Chief Assistant Analyst at the works of the Wolseley Motor Co., Ltd. (*Signed by*) J. E. Stead, H. Frankland, Ernest W. Jackson, *N. D. Ridsdale*, *C. H. Ridsdale*.

Wood, Charles Edmund, 83, Kingswood Road, Moseley, Birmingham. Research Chemist. B.Sc., 1914; M.Sc., 1915, obtained at University of Birmingham. Engaged on Chemical Research with Professor P. F. Frankland, F.R.S., from 1914–1917. (*Signed by*) Percy F. Frankland, Adrian J. Brown, Frederick Challenger, W. E. Garner, Geo. King, *Oscar L. Brady*.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, February 7th, 1918, at 8 p.m., Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Richard Lilburn Barnes	Dec. 2nd, 1875.	Jan. 30th, 1918.
John Forbes Bell	Dec. 5th, 1907.	Sept. 25th, 1917.
John Scudamore Sellon	Apr. 15th, 1875.	Jan 18th, 1918.

Certificates were read for the first time in favour of:

Thomas Thompson Best, Ph.D., "Woodleigh," Laurel Road, St. Helens.
Rudolph Isaac Blackburn, B.A., B.Sc., 8, Dunlace Road, Clapton, E.5.
Cyril Bride, B.A., B.Sc., 86, Ridgeway, Edgbaston, Birmingham.
Giuseppe Bruni, Prof., Corso Buenos Ayres, 55, Milan.
Colin Campbell, M.Sc., 45, Heywood Street, Alexandra Park, Manchester.
John George Clarke, M.A., B.Sc., 12, Rhodesia Road, Leytonstone, E.11.
Frederick Charles Duggleby, 87, Loughborough Park, Brixton, S.W.9.
Francis John Dymond, B.Sc., 6, Lockyer Street, Plymouth.
Owen Charles Edwards, B.Sc., 46, Saxon Road, Faversham.
Thomas Greetham, Finch Villa, Millom, Cumberland.
Henry Francis Everard Hulton, F.I.C., 15, Oakhill Court, East Putney, S.W.15.
Julius Jung, 14, Bancroft Road, E.1.
Benjamin Llewellyn, M.Sc., Lt., A.O.D., 11, St. Silas Street, Ardwick, Manchester.
William Alexander Montagu, Lt., H.L.I., 7, Garturk Street, Crosshill, Glasgow.
Harry Singer, 147, Upper Clapton Road, E.5.

Maurice Smith, J.P., c/o Messrs. Cuxson, Gerrard and Co., Ltd., Oldbury.
Stephen Veitch Telfer, M.B., Ch.B., 533, Crosshill Road, Crosshill, Glasgow.
Walter Arthur Voss, "Fairlight Glen," Eastwood Road, Rayleigh, Essex.
Harry William Webb, M.Sc., 29, South Road, Smethwick, B.O., Staffs.
James Wood, M.A., B.Sc., c/o Research Department, C.W.S., 109, Corporation Street, Manchester.

The following papers were read:

"Some inorganic stannichlorides." By J. G. F. Druce.
"A reinvestigation of the cellulose–dextrose relationship." By Miss M. Cunningham. (Read by Mr. C. F. Cross.)
"Esparto-cellulose and the problem of constitution." By C. F. Cross and E. J. Bevan.

Erratum.

In Proceedings for January 17th, 1918, add the following:

The following paper was read:

"Studies on the Walden inversion. Part VII. The influence of the solvent on the sign of the product in the conversion of α-bromo-β-phenylpropionic acid to α-amino-β-phenylpropionic acid (phenylalanine). Iminodiphenyldipropionic acid." By G. Senter, H. D. K. Drew, and G. H. Martin.

Ordinary Scientific Meeting, Thursday, February 21st, 1918, at 8 p.m., Professor W. J. Pope, C.B.E., F.R.S., President in the Chair.

Messrs. R. I. Phipps and A. S. Carlos were formally admitted as Fellows of the Society.

Certificates for Election were read for the first time in favour of:

Albert Henry Clark, B.Sc., 701, S. Wood Street, Chicago, U.S.A.
Horace George Evans, B.A., B.Sc., 393, City Road, Edgbaston, Birmingham.
Charles Eddie Gallagher, The Vestry House, St. Magnus-the-Martyr, Lower Thames Street, E.C.3.
Nathaniel Makover, B.Sc., 13, Bancroft Road, E.1.
Alexander Lyle Thomson, 11, Beresford Gardens, Trinity, Edinburgh.
Herbert John Watson, 64, Peel House Lane, Widnes.

A Certificate for election has been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of :

Stanley Warburton, Titaghur Paper Mills Co., Ltd., Titaghur, India.

It was reported that Mr. Thomas Tyrer, who was elected a Fellow in 1876, died on February 21st, 1918.

The PRESIDENT announced that the following changes in the Officers and Council were proposed by the Council:

As Vice-Presidents to retire.—Professor F. R. Japp and Sir Richard Threlfall.

As Ordinary Members of Council to retire.—Rt. Hon. The Earl of Berkeley, Professor H. C. H. Carpenter, Dr. R. H. Aders Plimmer, and Professor J. F. Thorpe.

As President.—Professor William Jackson Pope.

As Vice-Presidents who have filled the office of President.—Professor H. E. Armstrong, Professor A. Crum Brown, Sir William Crookes, Sir James Dewar, Professor Harold B. Dixon, Professor Percy F. Frankland, Dr. A. G. Vernon Harcourt, Professor W. Odling, Professor W. H. Perkin, Professor J. Emerson Reynolds, Dr. Alexander Scott, Sir Edward Thorpe, and Sir William A. Tilden.

As Treasurer.—Dr. M. O. Forster.

As Honorary Secretaries.—Dr. Samuel Smiles and Professor J. C. Philip.

As Foreign Secretary.—Lt.-Colonel Arthur W. Crossley.

As Vice-Presidents.—Professor F. G. Donnan, Professor G. G. Henderson, Professor A. Lapworth, Lt.-Col. A. Smithells, Professor W. P. Wynne, and Professor S. Young.

As New Ordinary Members of Council.—Mr. J. L. Baker, Professor J. C. Irvine, Sir Herbert Jackson, and Mr. E. W. Voelcker.

Mr. C. F. Cross, Dr. C. A. Keane, and Mr. E. W. Voelcker, were elected Auditors to audit the Society's Accounts.

Messrs. R. E. Jackson and P. T. White were elected Scrutators

and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

Ernest Atkinson.
Charles Frederick Lee Barber.
Albert Leslie Bloomfield, B.A.
John Boothman
Joseph William Christelow, B.Sc.
Edgar Alfred Coakill.
Ransome Wallace Cooper.
Thomas Crowdy.
Harry Dugald Keith Drew, B.Sc.
John Clare Newlands Eastick.
Frederick William Edwards.
Thomas Gifford Elliot.
Frederick William Emerson.
Frederick Page Evans, B.Sc.
Charles Henry Fielding.
Robert Fleming, B.A.
Thomas Frazer, B.A.
Frederic Horace Garner, M.Sc.
Cecil Stevenson Garnett.
Julius Geldard.
William Frank Grant, B.Sc.
William Robinson Grist.
Francis Clint Guthrie, B.A.
Joseph Eli Hanson.
Ernest Hardiker.
Alan Haythornthwaite, B.Sc.
Thomas John Hitchcock.
Harold Housley, M.Sc.
Owen Rhys Howell, B.Sc.
William Earl Hughes.
Herbert Spencer Kipling.
Thomas Williamson Kirkwood, B.Sc.
Kumudchandra Ghelabhai Laiwala, M.A., B.Sc.
Harold Lawrence.
Francis Charles Lewis, B.Sc.
Arnold Bradley Lowndes.
William Jackson Lund, M.Sc. Tech.
Archibald Bruce Macallum.
Alfred Bertram Mann.
Elias Mendoza.
John Richard Morgan, B.Sc.
Arthur Macdonald Munro, M.A.
Theketh Kumaran Nair, B.A., B.Sc.
Robert Atkinson Oddy.
Horace Finningley Oxley, B.A.
Henri Marc Pezzani.
David John Prichard Phillips, B.Sc.
Tudor Williams Price, B.A., M.Sc.
Robert Ray, B.Sc.
Ferdinand Roques.
Alfred Ulrich Max Schlaepfer, D.Sc. Tech.
William Leonard Scotcher.
Harold Pethick Shilston.
Snow Blagburn Tallantyre, B.Sc.
George Taylor.
John Cameron Clarke Taylor.
Hugh Arwel Thomas, B.Sc.
Albert Edward Timmins
John Trotter, M.A., D.Sc.
George Johnston Twine.
Leonard Ellerton Vlies.
Glen Raymond Wakeham, B.Sc.
Godfrey Warburton.
Harry Wignall, M.Sc.
Arthur William Willis.
Charles Edmund Wood, M.Sc.

Professor the Hon. R. J. Strutt, F.R.S., then delivered his lecture, entitled "Recent Studies on Active Nitrogen." A vote of thanks proposed by Dr. A. Scott, seconded by Professor Findlay, and supported by the President was carried with acclamation.

ANNUAL GENERAL MEETING.

The Annual General Meeting will be held on Thursday, March 21st, 1918, at 4.30 p.m., when the PRESIDENT will deliver his Address. There will be an Informal Meeting the same evening after the conclusion of the formal business of the Ordinary Scientific Meeting to be held at 8 p.m. The Council will gladly welcome assistance from any Fellows who are able to increase the scientific interest of the Informal Meetings by showing experiments or apparatus, and all offers of such assistance should be made to the Assistant Secretary not later than the Monday previous to the meeting.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

MOORE, HAROLD. Liquid fuels for internal combustion engines. London 1918. pp. xv + 200. 12*s*. 6*d*. net. (*Recd*. 6/2/18.)

From the Publishers: Messrs. Crosby, Lockwood and Son.

REMINGTON, JOSEPH P., and COOK, E. FULLERTON. The practice of pharmacy. A treatise on the modes of making and dispensing official, unofficial, and extemporaneous preparations, with descriptions of medicinal substances, their properties, uses, and doses. 6th edition. Philadelphia 1917. pp. xviii + 1987. ill. 35*s*. net. (*Recd*. 8/2/18.)

From the Publishers: Messrs. The J. B. Lippincott Company.

SMITH, GEORGE. The laboratory, or school of arts. A variety of curious and valuable experiments in refining, . . . choice secrets of jewellers, . . . casting, . . . the art of making glass, etc. [Compiled from German and other foreign authors.] London 1738. pp. x + 242 + vi. (*Reference*.) From Dr. E. F. Armstrong.

II. *By Purchase.*

AMAGAT, E.-H., and DÉCOMBE, L. La statique des fluides la liquéfaction des gaz et l'industrie du froid. (Encyclopédie de

science chimique appliquée. Vol. 7.) Paris 1917. ill. pp. vi + 265. 14*s.* net. (*Recd.* 1/2/18.)

Calvert, Gascoigne T. The manufacture of sulphate of ammonia and crude ammonia. 2nd edition. London 1917. pp. xii + 153. ill. 7*s.* 6*d.* net. (*Recd.* 13/2/18.)

Christopher, J. E. Modern coking practice. Including the analysis of materials and products by Thomas Henry Byrom. 2nd edition. London 1917. 2 vols. pp. xii + 106, 124 ill. 15*s.* net. (*Recd.* 13/2/18.)

Dumesny, P., and Noyer, J. Wood-products, distillates and extracts. Translated by Donald Grant. London 1908. pp. xvi + 320. ill. 10*s.* 6*d.* net. (*Recd.* 13/2/18.)

Goulding, Ernest. Cotton and other vegetable fibres: their production and utilisation. London 1917. pp. x + 231. ill. 6*s.* net. (*Recd.* 13/2/18.)

Jones, Harry C. The nature of solution. With a biographical sketch by E. Emmet Reid. London (printed in the U.S.A.) 1917. ill. pp. xxiii + 380. 12*s.* 6*d.* net. (*Recd.* 17/12/17.)

Loeb, Jacques. The organism as a whole from a physico-chemical viewpoint. New York 1916. pp. x + 379. ill. 12*s.* 6*d.* net. (*Recd.* 13/2/18.)

Lusk, Graham. The elements of the science of nutrition. 3rd edition. Philadelphia 1917. pp. 641. ill. 20*s.* net. (*Recd.* 13/2/18.)

Millikan, Robert Andrews. The electron, its isolation and measurement, and the determination of some of its properties. Chicago 1917. pp. xii + 268. ill. 7*s.* net. (*Recd.* 13/2/18.)

Ostwald, Wolfgang. An introduction to theoretical and applied colloid chemistry. Translated by Martin H. Fischer. New York 1917. pp. xv + 232. ill. 11*s.* 6*d.* net. (*Recd.* 13/2/18.)

Pickering, George Fenwick. Aids to the commercial analysis of oils, fats, and their commercial products. A laboratory handbook. London 1917. pp. viii + 133. 7*s.* 6*d.* net. (*Recd.* 13/2/18.)

Price, William B., and Meade, Richard K. The technical analysis of brass and the non-ferrous alloys. 2nd edition. New York 1917. 13*s.* 6*d.* net.

Scherer, Robert. Casein, its preparation and technical utilisation. Translated by Charles Salter. 2nd edition. London 1911. pp. xi + 182. ill. 7*s.* 6*d.* net. (*Recd.* 13/2/18.)

Schuster, Arthur, and Shipley, Arthur E. Britain's Heritage of Science. London 1917. pp. xv + 334. ill. 8*s.* 6*d.* net. (*Recd.* 13/2/18.)

Tognoli, Edgardo. Reagents and reactions. Translated by C. Ainsworth Mitchell. London 1918. pp. viii + 228. 6*s*. net. (*Recd.* 13/2/18.)

Villavecchia, Vittorio [& others]. Treatise on applied analytical chemistry. Methods and standards for the chemical analysis of the principal industrial and food products. Translated by Thomas H. Pope. Vol. I. London 1918. pp. xvi + 475. ill. 21*s*. net. (*Recd.* 13/2/18.)

Ullmann, Fritz [Editor]. Enzyklopädie der technischen Chemie. Vols. 1 to 4. A. to Essigäther. Berlin 1914—1916. ill. pp. x + 814, 800, 808, 791. (*Reference.*)

Wallis-Tayler, A. J. The preservation of wood. A descriptive treatise on the processes and the mechanical appliances used for the preservation of wood. London 1917. pp. xix + 344. ill. 10*s*. 6*d*. net. (*Recd.* 13/2/18.)

Warnes, Arthur R. Coal tar distillation and working up of tar products. 2nd edition. London 1917. pp. xii + 302. ill. 10*s*. 6*d*. net. (*Recd.* 13/2/18.)

Zsigmondy, Richard. The chemistry of colloids. Part I. Kolloidchemie, by R. Z., translated by Ellwood B. Spear. Part II. Industrial colloidal chemistry, by Ellwood B. Spear. With a chapter on colloidal chemistry and sanitation, by John Foote Norton. New York 1917. pp. vii + 288. 13*s*. 6*d*. net. (*Recd.* 13/2/18.)

III. *Pamphlets.*

Scientific and Industrial Research, Committee of the Privy Council for. Reports . . . for the years 1915—1916 and 1916—1917. London 1916. pp. 56, 63.

Scientific and Industrial Research, Committee of the Privy Council for. Report of the Fuel Research Board on their scheme of research and on the establishment of a Fuel Research Station. London 1917. p. 10.

Scientific and Industrial Research, Department of. Science and Industry, a series of papers bearing on industrial research. Number 1. Industrial research in the United States of America. By A. P. M. Fleming. London 1917. pp. viii + 60. ill.

Shaw, Peter, and Hauksbee, Francis. Proposals for a course of chemical experiments: with a view to practical philosophy, arts, trades, and business. London, May 12th, 1731. p. 8.

Travers, Morris W., Gupta, N. M., and Ray, P. C. Some compounds of boron, oxygen, and hydrogen. London 1916. pp. 46.

WAHL, ROBERT. New scientific conceptions and their application to quality and methods of preparing beer. Collated from four lectures delivered before the Master Brewers' Association of the United States. (From the *Amer. Brewers' Rev.*, 1915.)

ZAMBONINI, FERRUCCIO. Sulle soluzioni solide, dei composti di calcio, stronzio, bario e piombo con quelli delle "terre rare" e loso importanza per la Mineralogia Chimica. (From the *Rivista Min. e Crist. Ital.*, 1915, **45**.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, March 7th, 1918, at 8 p.m., Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	*Died.*
Arthur Clegg Bowdler	April 20th, 1865	Feb. 17th.
Egerton Hargreaves	May 6th, 1909	„ 14th
Edmund Arthur Letts	Feb. 6th, 1879	„ 19th.

Messrs. G. Taylor, J. R. Morgan, T. W. Kirkwood, and G. Warburton were formally admitted Fellows of the Chemical Society.

The names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council for 1918–1919 were read from the Chair.

The PRESIDENT announced that owing to the need for economy in the use of paper, the Council had decided not to provide each Fellow with a copy of the Report of Council, but that any Fellow wishing to consult the Report could do so by applying to the Assistant Secretary.

Certificates were read for the first time in favour of:

George Edwin Anderson, B.Sc., 247, John Williamson Street, South Shields,
James Booth, 18, Wilfred Street, Derby.
Stanley Dixon, M.Sc., 17, Morton Terrace, Gainsborough.
Arthur Geake, M.Sc., No. 1, Staff House Eastriggs, Dumfriesshire.
William Hughes, 63, Goldington Avenue, Bedford.

Stewart Roy Illingworth, B.Sc., A.R.C.S., Fern Villa, Chesham Bois, Chesham.
George Johnson, 4, Birch Grove, Weaste, Manchester.
Robert Duncan Masson, 13, Westbourne Grove, West Kirby, Birkenhead.
Harold Scragg, Post Office, St. Anthony's, Newcastle-upon-Tyne.
David Dryden Spence, Risca, Woodbine Avenue, Gosforth, Newcastle-upon-Tyne.
William Edwin Upton, M.A., 663, Leigh Road, Leigh.
Thomas Wallace, M.Sc., 307, Beaconsfield Street, Newcastle-upon-Tyne.
Henry Worth, 70, Vyner Street, York

A Certificate for election has been authorised by the Council for presentation to ballot under Bye-law I(3) in favour of:

Govindra Chandra Das, B.Sc., 20, Sunker Ghose Lane, Calcutta.

The following papers were read:

"Atomic and molecular numbers." By H. S. Allen.
"The alkaloids of ipecacuanha. Part III." By F. L. Pyman.

Ordinary Scientific Meeting, Thursday, March 21st, 1918, at 8 p.m., Professor W. J. Pope, C.B.E., F.R.S., President, in the chair.

The President referred to the loss sustained by the Society, through death on February 22nd, 1918, of Mr. Thomas Charles Cloud, who was elected a Fellow on February 7th, 1878.

Certificates were read for the first time in favour of:

Wilfred John Brizell, 20, Cromer Drive, Wallasey, Cheshire.
James Scott Dick, B.Sc., 93, Wellmeadow Road, Catford, S.E. 6.
John Henry Freeman, 2, Park Road, Stratford-le-Hope, Essex.
Archibald Edwin Goddard, B.Sc., "The Osborne," Irvine.
Robert John Hughes, B.Sc., Lakefield House, Llanelly.
Harold Thomas Islip, A.I.C., "Stilton," St. Mark's Road, Maidenhead.
George Turpin Moore, B.Sc., 19, Neale Street, Roker, Sunderland.
George Newbery, B.Sc., A.R.C.S. "Glenmore," Balcombe, Haywards Heath.
William Charles Peck, 20, Bassano Street, East Dulwich, S.E., 22.
Arthur Nutter Smith, 47, North Road, West Bridgford, Nottingham.
John Henry Taylor, 56, Highbury, Newcastle-upon-Tyne.
Thomas Tucker, 2, York Villas, Queen's Road, Buckhurst Hill, Essex.
Augustus James Tyrrell, 11, Holdenhurst Road, Bournemouth.
Arthur Robert Warnes, 47, Cranbrook Avenue, Cottingham Road, Hull.

The meeting was then adjourned and the Informal Meeting declared open.

HUGO MÜLLER LECTURE.

The next Ordinary Scientific Meeting will be held on Thursday, April, 18th, 1918, at 8 p.m., when Sir Henry Miers, F.R.S., will deliver the Hugo Müller Lecture entitled: "The Old and the New Mineralogy."

ADDITIONS TO THE LIBRARY.

I. *Donations.*

KINGZETT, CHARLES THOMAS. Chemistry for beginners and schoolboys. 2nd edition. London 1918. pp. viii + 150. 2*s.* 6*d.* net. (*Recd.* 15/2/18.) From the Author.

PILCHER, RICHARD B., and BUTLER-JONES, FRANK. What industry owes to chemical science. London. 1918. pp. xiv + 150. 3*s.* net. (*Recd.* 14/3/18.) From the Publishers: Messrs Constable & Co. Ltd.

WORDEN, EDWARD CHAUNCEY. Technology of cellulose esters. Vol. VIII. Carbohydrate carboxylates (cellulose acetate). New York 1916. pp. xxxvi + 2501–3078 ill. $5 net. (*Recd.* 1/3/18.) From the Author.

II. *By Purchase.*

BINGHAM, CHARLES. The manufacture of carbide of calcium. London 1916. pp. iv + 219. ill. 7*s.* 6*d.* net. (*Recd.* 7/3/18.)

FRIEND, J. NEWTON [Editor]. A text-book of inorganic chemistry. Vol. V. Carbon and its allies. By ROBERT MARTIN CAVEN. London 1917. pp. xxi + 468. 15*s.* net. (*Reference.*)

HEFTER, GUSTAV. Technologie der Fette und Oele. Vol. II. Berlin 1908. pp. x + 974. ill. (*Recd.* 23/2/18.)

JELLINEK, KARL. Lehrbuch der physikalischen Chemie. Vol. II. Stuttgart 1915. pp. xii + 939. ill. (*Recd.* 27/2/18.)

MARTIN, GEOFFREY. Industrial and manufacturing chemistry. Part II. Inorganic. Vol. ii. London 1917. pp. xvi + 482. ill. 25*s.* net. (*Recd.* 13/2/18.)

III. *Pamphlets.*

BACKER, HILMAR JOHANNES. Oude chemische werktuigen en laboratoria van Zosimos tot Boerhaave. Groningen 1918. pp. 68.

BOSWELL, P. G. H. A supplementary memoir on British resources of sands and rocks used in glass manufacture, with notes on certain

refractory materials. With contributions by W. B. WRIGHT, HENRY FRANCIS HARWOOD, and ARTHUR ALFRED ELDRIDGE. London 1917. pp. 92.

CHAPMAN, C. E. Bonedust: its adulteration with phosphate rock (*S. Australia, Dept. of Chem. Bull.*, 1917. No. 9).

EASTMAN KODAK COMPANY. Abridged scientific publications from the Research Laboratory. Vol. II. 1915–1916. Rochester, New York, 1917. pp. 134.

GHOSH, JNANENDRA CHANDRA. On a new method of preparing colloids. (From the *Rep. Indian Assoc. Sci.*, 1915.)

HARGREAVES, WILLIAM ARTHUR. Lecture on chemical research in relation to industry. Adelaide 1917. pp. 35.

HENDRICK JAMES. The growth of International trade in manures and foods. (From the *Trans. Highland and Agric. Soc. Scotland.*)

IMPERIAL INSTITUTE. Zinc ores. (Monographs on mineral resources with special reference to those of the British Empire). London 1917. pp. 64.

MOIR, JAMES. Colour and constitution. Part II. The spectra of the mixed phthaleins and of the sulphone-phthaleins. (From the [*Minutes of*] *Roy. Soc. S. Africa.* 1917.]

SOSMAN, R. B., and HOSTETTER, J. C. The ferrous iron-content and magnetic susceptibility of some artificial and natural oxides of irons. (From the *Bull. Amer. Inst. Min. Eng.*, 1917.)

——— Zonal growth in hematite, and its bearing on the origin of certain iron ores. (From the *Bull. Amer. Inst. Min. Eng.*, 1917.)

SPRIGGS, E. J., and WEIR, A. B. The digestibility of bread made from two parts of wheat and one part of oats, barley, maize or rice. (From *The Lancet*, 1917).

WINTERBOTTOM, D. C. Gypsum and plaster of Paris. (*S. Australia, Dept. of Chem. Bull.*, 1917, No. 7.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, April 18th, 1918, at 8 p.m., Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Killed in Action.
Leonard Ison Pitt	Nov. 15th, 1911.	July 30th, 1915.

	Elected.	Died.
Edward Francis	Dec. 18th, 1879.	Mar. 30th.
George Thomas Glover	Jan. 18th, 1872.	
Henry James Helm	Jan. 18th, 1872.	Mar. 24th.
William Joel Kemp	May 4th, 1882.	Mar. 22nd.
Joseph Price Remington	July 17th, 1886.	Jan. 1st.
Alfred Gordon Salamon	Feb. 19th, 1880.	April 9th.
Edward Cumming Thompson ...	June 7th, 1894.	April 9th.

It was announced that the following Committees for 1918—1919 had been appointed by the Council:

Finance Committee.—Messrs. E. G. Hooper, G. T. Moody, Sir E. Thorpe, Sir William A. Tilden, and the Officers.

House Committee.—Messrs. R. Messel, J. E. Reynolds, Alexander Scott, J. M. Thomson, Sir William A. Tilden, and the Officers.

Library Committee.—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, T. M. Lowry, J. M. Thomson (chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

Publication Committee.—Messrs. A. Chaston Chapman, A. Harden, T. A. Henry, C. A. Keane, G. T. Morgan, F. L. Pyman, Alexander Scott, J. F. Thorpe, and the Officers.

Research Fund Committee.—Messrs. E. C. C. Baly, F. H. Carr, D. L. Chapman, H. J. H. Fenton, F. S. Kipping, A. Lapworth, W. H. Perkin, Alexander Scott, J. F. Thorpe, W. P. Wynne, and the Officers.

Messrs. M. Schlaepfer, H. A. Thomas, and W. D. Craddon were formally admitted as Fellows of the Chemical Society.

Certificates for Election were read for the first time in favour of:

George Henry Rowland Barham, 74, Kensington Avenue, Manor Park, E.12.
Henry Aldons Bromley, The Willow, Cambridge Road, W. Wimbledon, S.W.19.
Joseph William Bell, 130, Manchester Road, Burnley.
Albert Eric Cashmore, 32, Vicarage Road, Smethwick, BO., Staffs.
Hubert William Dailey, 19, Beverley Road, Anerley, S.E.
Arthur Broughton Edge, Tudor House, Maidenhead.
Francis William FitzGerald, 128, Earlham Grove, Forest Gate, E.7.
Nalini Mohan Gupta, M.Sc., Panposh, B.N. Railway, India.
Ernst Johannes Hartung, M.Sc., 9, Glendearg Grove, Malvern, Melbourne, Australia.
Ben Lockspeiser, M.A., 21 Thornby Road, Clapton, E.5.
Edgar Newbery, D.Sc., The University, Manchester.
Edward Chuston Powell, 39, Lombard Street, E.C.3.
Runar Ivar Olsson-Seffer, 1, Royal Exchange Place, Calcutta, India.
Alan Speedy, 81 Burges Road, East Ham, E.6.
John Thomas, B.A., D.Sc., Solway Dyes Co., Humell Hill Works, Carlisle.
Hubert Charles Siegfried de Whalley, 18, Brandram Road, Lee, S.E.13.
William Whyte, 98, Kirkmanshulme Lane, Longsight, Manchester.
Samuel Walter Woolley, 58, North Hill, Highgate, N.6.

A Certificate for Election has been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of:

William Jay Hale, University of Michigan, Ann Arbor, Michigan.

The first of the Hugo Müller Lectures was then delivered by Sir Henry Miers, F.R.S., who discoursed on "The Old and the New Mineralogy." A vote of thanks to Sir Henry Miers for his Lecture was proposed by Professor H. E. Armstrong and seconded by Sir William A. Tilden, acknowledgment being made by the Lecturer.

ORDINARY SCIENTIFIC MEETING.

The next Ordinary Scientific Meeting will be held on Thursday, May 2nd, at 8 p.m., when a ballot for the election of Fellows will be held.

INFORMAL MEETING.

The next Informal Meeting of the Society will be held on Thursday, May 16th, after the conclusion of the formal business of the Ordinary Scientific Meeting to be held at 8 p.m.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W., must be received on or before Monday, June 3rd, 1918.

All persons who received grants in June, 1917, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be returned by Saturday, June 1st, 1918.

The Council wish to direct attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

BLASDALE, WALTER C. Principles of quantitative analysis. An introductory course. 2nd edition. London 1917. pp. xii + 402. ill. 10*s*. 6*d*. net. (*Recd.* 10/4/18.)

From the Publishers: Messrs. Constable and Co.

GOWLAND, WILLIAM. The metallurgy of the non-ferrous metals. 2nd edition. London 1918. pp. xxxi + 588. ill. 25*s*. net. (*Recd.* 27/3/18.) From the Author.

MACLEAN, HUGH. Lecithin and allied substance. The lipins. London 1918. pp. vi + 206. 7*s*. 6*d*. net. (*Recd.* 26/3/18.)

From the Publishers: Messrs. Longmans, Green and Co.

WOODWARD, CHARLES JOSIAH. ABC five-figure logarithms and tables for chemists, including electro-chemical equivalents, analytical factors, gas reduction tables, and other tables useful in

chemical laboratories. New edition. London 1917. pp. 76. 3s. net. (*Reference.*)

From the Publishers: Messrs. E. and F. N. Spon.

II. *By Purchase.*

Abel, Emil. Hypochlorite und elektrische Bleiche. Theoretischer Teil. (Monograph. angew. Elektroch., vol. 17.) Halle a. S. 1905. pp. 111. ill.

Becker, H. Die Elektrometallurgie der Alkalimetalle. (Monograph. angew. Elektroch., vol. 9.) Halle a. S. 1903. pp. 135. ill.

Cowper-Coles, Sherard. Elektrolytisches Verfahren zur Herstellung parabolischer Spiegel. (Monograph. angew. Elektroch., vol. 14.) Halle a. S. 1904. pp. 17. ill.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY MEETING ON THURSDAY, MAY 2nd, 1918.

N.B.—The names of those who sign from "General Knowledge are printed in *italics*.

Anderson, George Edwin, 247, John Williamson Street, South Shields. Works Chemist. Walker and Wallsend Union Gas Company. 1st Class Hons., Oxford Senior (including Chemistry); three years Armstrong College, Durham University; Bachelor of Science Degree (Chemistry and Geology). Engaged in Research and Supervision of Plant for Benzol Recovery. (*Signed by*) P. Phillips Bedson, J. A. Smythe, F. G. Henderson, *Frederick N. Binks, J. T. Dunn.*

Best, Thomas Thompson, Ph.D., "Woodleigh," Laurel Road, St. Helens. Alkali Works Manager. 1883–6, three years' Chemical Course at Victoria University under Profs. Roscoe, Schorlemmer, and Balfour Stewart. Claisen Prize of £25 for research on "The Spectroscopic Determination of the Fixed Gases in One Another." 1886–1888, two years at Erlangen University under Prof. Otto Fischer; obtained degree of Ph.D. for research "Ueber das Orthoanisidin." 1888–9, Lecturer in Organic and Applied Chemistry at Manchester Technical Schools. 1889 to present, Chief Chemist and Manager of the Hardshaw Brook Works of the United Alkali Co., Ltd., St. Helens. Since 1892 I have brought out the following Processes and Patents:—Apparatus for Elevating Corrosive Liquids: Patent No. 17593; 1894. Apparatus for Drying Crystals: kept secret. Apparatus for Slaking Lime: Patent No. 10723; 1902. Improvements in Burning Pyrites: Patent No. 7915; 1905. Process for making Calcium Chloride from the Waste Liquors of the Chlorate of Potash Manufacture: kept secret. Process for manufacturing Chlorate of Soda from Carbonate of Soda: Patent No. 19198;

1894. Improvement in the Manufacture of Chlorine: Patent No. 13461; 1895. An improved Process for the Manufacture of Matches: Patent No. 104015; 1916. (*Signed by*) J. W. Kynaston, John W. Towers, H. A. Auden, A. Holt, E. C. C. Baly, A. J. Squires, *J. H. Wigner.*

BLACKBURN, RUDOLPH ISAAC, 8, Dunlace Road, Clapton, London, E.5. Analytical and Technical Research Chemist. B.A. Hons., Cantab; B.Sc. Hons., Lond.; 1st Class Hons. in Natural Sciences Tripos, Part I., 1910; 2nd Class Hons. in Natural Sciences Tripos, Part II. (Chemistry), 1911; 1st Class Hons. in Chemistry in B.Sc., Lond., 1911. Formerly Lecturer in Chemistry at Tottenham Polytechnic. For three years I was on the Technical Staff of Messrs. Boult, Wade and Tennant, Chartered Patent Agents, where I was engaged on chemical work in relation to patents. Since 1916 I have been engaged as a Technical Research Chemist at the Osram-Robertson Lamp Works, Hammersmith, W. (*Signed by*) Joseph S. Bridges, W. J. Pope, H. J. H. Fenton, Ernest Fyleman, *Horatio Ballantyne.*

BOOTH, JAMES, 18, Wilfred Street, Derby. Chemist. Studied Chemistry under Mr. G. Guest, B.Sc. (Vict.) for six years. Qualified for the Scholastic Profession under the Board of Education. Assistant to Mr. J. W. Goodyere, B.Sc. (Lond.), Chemical Laboratories, Grimsby Municipal College. Chemist in employ of Staveley Coal and Iron Co., Ltd., Chesterfield. Chemist in employ of Messrs. Turner Bros., Asbestos Co., Trafford Park, Manchester. Chemist in employ of Clayton Aniline Co., Ltd., Manchester. Chemist in employ of British Cellulose and Chemical Manufacturing Co., Ltd., Spondon. (*Signed by*) W. H. Bentley, John H. Jeffery, Wm. P. Skertchly, H. H. H. Lorenz, Robert Dodd.

BRIDE, CYRIL, 86, Ridgeway, Edgbaston, Birmingham. B.A. (Oxford), 2nd Class Honours, Chemistry Finals, 1914; B.Sc. (London), 1st Class Honours, Chemistry Finals, 1914. Process Chemist, Messrs. Chance and Hunt, Ltd., from August, 1915, to September, 1916; Chemist-in-Charge from September, 1916. (*Signed by*) R. E. Forbester, Conrad H. Rogers, F. P. Dunn, H. E. Smith, R. W. L. Clarke.

BRIZELL, WILFRID JOHN, 20, Cromer Drive, Wallasey, Cheshire. Works Chemist and Analyst. Three years' training (1906–1909) Liverpool Technical School; five years (1910–1915) at Municipal Technical School, Bootle, Lancs.; Courses on Organic, Inorganic, and Analytical Chemistry up to Final B.Sc. standard; seven years' (1910–1917) works experience at Calthrop Bros., Ltd., of 56 Naylor Street, Liverpool, Manufacturer of Compound Feeding Cakes and Meals, where I was in charge of the Chemical Laboratories, and was responsible for the large amount of analytical work and research work undertaken. In July, 1917, was appointed Works Chemist and Analyst to the Co-operative Wholesale Society's African Oil Mills, Liverpool, where I am in full control of all the chemical work (analytical and research) connected with oils and feeding cakes. Co-patentee for process for refining Cocoa Butter. (*Signed by*) Geoffrey Martin, C. Polychronis, W. R. Ormandy, *George Senter, Fred Barrow.*

BRUNI, GIUSEPPE, Corsa Buenos Ayres, 55, Milan (Italy). Professor of General Chemistry at the R. Polytechnic, Milan. Formerly Professor of General Chemistry at the University of Padua. Investigations on various subjects in Physical and Inorganic Chemistry, particularly on Solid Solutions and allied subjects, (*Signed by*) N. T. M. Wilsmore, F. G. Donnan, Cecil H. Desch, *G. G. Henderson, H. C. H. Carpenter.*

CAMPBELL, COLIN, M.Sc., 45, Heywood Street, Alexandra Park, Manchester.

Assistant Lecturer and Demonstrator in Chemistry in the University of Manchester. Part-author of the following papers: "Photographic Analysis of Explosions in the Magnetic Field," *Proc. R.S.*; "The Firing of Gases by Adiabatic Compression, Part I.," *Trans. Chem. Soc.*, with Prof. H. B. Dixon; "The Preparation and Analysis of Methane," *Trans. Chem. Soc.*, with Dr. A. Parker; "Conditions affecting Explosions," *J. Soc. Chem. Ind.*, with E. L. Sellars. (*Signed by*) Harold B. Dixon, Arthur Lapworth, F. P. Burt, W. K. Slater, Norman Smith, J. E. Myers.

Clark, Albert Henry, Ph.G., B.Sc., 701 S, Wood Street, Chicago, Ill., U.S.A. Assistant Professor, Assistant Instructor, etc., U. of I. School of Pharmacy, 1905 to present time. Registered Pharmacist in Illinois, 1892, to present time. Chemist for American Medical Association, 1906–1911. Murray Nickel Manufacturing Co., 1907–1909. Member of the American Chemical Society, American Pharmaceutical Association, American Association for Advancement of Science, Illinois Pharmaceutical Association, Alumni Associations University of Illinois and University of Michigan. Member Committee of Revision United States Pharmacopœia. Ex-Chairman Scientific Section and Ex-Secretary Historical Section American Pharmaceutical Association, Ex-President American Conference Pharmaceutical Faculties. (*Signed by*) Frederick B. Power, H. V. Arny, Virgil Coblentz, *A. B. Lyons*, *Wm. Jay Schieffelin.*

Clarke, John George, 12, Rhodesia Road, Leytonstone, E.11. Works Chemist, Messrs. Boake, Roberts and Berry. M.A. (St. Andrews) with 1st Class Honours in Final B.Sc. Chemistry; Lecture Assistant, St. Andrews, 1915–1918; Research Assistant, St. Andrews, 1916–1918. (*Signed by*) J. C. Irvine, W. N. Haworth, G. Robertson, John Anderson, R. C. Menzies.

Dick, James Scott, 93, Wellmeadow Road, Catford, S.E.6. Research Chemist. B.Sc. (St. Andrews), 1912; Higher Standard in Chemistry (with special distinction), Natural Philosophy, and Mathematics; Berry Scholar in Chemistry, 1912–1913; Carnegie Research Scholar, 1913–1915; Research Chemist, Research Department, Royal Arsenal, Woolwich, from 1915. (*Signed by*) Robert Robertson, J. C. Irvine, W. N. Haworth, William S. Denham, Irvine Masson, W. Howieson Gibson, H. Bassett, *E. F. Armstrong.*

Dixon, Stanley, 17, Morton Terrace, Gainsborough. Chief Assistant to Messrs. A. H. Allen and Partners, Public Analysts, Analytical and Consulting Chemists, 67, Surrey Street, Sheffield. M.Sc. (Sheffield); A.I.C. (*Signed by*) W. P. Wynne, S. Ernest Melling, W. E. S. Turner, John Evans, Jas. T. Stevenson, Arnold R. Tankard.

Duggleby, Frederick Charles, 87 Loughborough Park, Brixton, S.W. Analytical Chemist. To obtain your scientific literature. (*Signed by*) J. Langford Moore, Geo. H. Goddon, G. M. Williams, H. N. Davidge, *M. S. Salamon.*

Dymond, Francis John, 6 Lockyer Street, Plymouth. Chemist. Bachelor of Science (Bristol), Chemist-in-Charge, H.M. Factory. (*Signed by*) F. Francis, J. W. McBain, F. W. Rixon, H. W. Cremer, J. de Carle Smith, R. Barclay Craig.

Edwards, Owen Charles, 46, Saxon Road, Faversham, Kent. Works Chemist. B.Sc. (Wales); Chemist and Research Chemist to the Cotton Powder Co. (*Signed by*) Kennedy J. P. Orton, John O. Hughes, Harry Gollop, *Alex. Findlay, Claude M. Thompson.*

Evans, Horace George, 393 City Road, Edgbaston, Birmingham. Research Chemist, Messrs. Chance and Hunt. Birmingham University, B.Sc. Degree

(Honours Division); Oxford University, B.A. Degree, Final Honour School of Chemistry; King Edward VII. Grammar School, Coalville, Leicester; Science Master, 1912–1915; Chigwell School, Essex, 1915–1916; Liverpool College, 1916–1917; Messrs. Chance and Hunt, 1917–present time. (*Signed by*) D. L. Chapman, H. A. Scarborough, Frank E. Thompson, R. E. Forbester, J. Eric Collington.

FREEMAN, JOHN HENRY, 2 Park Road, Stanford-le-Hope, S.10. Chemist. Chief Chemist for Kynoch, Ltd., for the past six years. (*Signed by*) A. T. Cocking, H. M. Langton, N. A. Anfilogoff, *Harold J. Page*, *F. B. Thole*, *A. E. Dunstan*.

GALLAGHER, CHARLES EDDIE, The Vestry House, St. Magnus the Martyr, Lower Thames Street, London, E.C.3. Student, City and Guilds of London Institute Technical College, Finsbury, Leonard Street, London, E.C.2 Being a chemical student at the above-named college I am desirous of being in touch with the modern advances of chemistry; to be able to attend the Society's meetings, and to have the use of the library. (*Signed by*) G. T. Morgan, A. J. Hale, Percy Edgerton, William H. Prince, *Robt. G. Grimwood*.

GEAKE, ARTHUR, Eastriggs, Dumfriesshire. Research chemist. B.Sc. (Bristol); 1st Class Hons. in Chemistry, 1910; M.Sc. (Bristol), 1911. From 1911–1914, carried out research work for Board of Agriculture and Fisheries; from 1915 to present time, Chemist in the Department of Explosives Supply. (*Signed by*) Hubert E. Page, E. Taberner, John Mitchley, Douglas Bowack, J. C. Burnham, *David Hooper*.

GODDARD, ARCHIBALD EDWIN, "The Osborne," Irvine, Ayrshire. Chemist, Noble's Explosive Co. Three years' course at University of Birmingham; B.Sc. (Birm.); 1916–1918, Research and Works Chemist with the above company. (*Signed by*) Wm. Rintoul, Wm. Barbour, William Dickson, Edward Wheeler, T. W. Price.

GREETHAM, THOMAS, Finch Villa, Millom, Cumberland. At present superintending the manufacture of pig-iron to specified analyses (special hematite). Four blast furnaces. Training: private. Experience: For the last fifteen years chief chemist for the Millom and Askam Hematite Iron Co., Ltd., the largest producers of hematite pig-iron for the open market on the West Coast. (*Signed by*) R. R. Tatlock, R. T. Thomson, Alex. W. McLaren, *W. T. Thomson*, *J. Reilly*.

HUGHES, ROBERT JOHN, Lakefield House, Llanelly. B.Sc. (Wales); Trained at University College of North Wales, Bangor; B.Sc. (Wales), 1912. Final subjects: Chemistry (Organic and Inorganic), and Mathematics (Pure and Applied). Chemistry and Maths. Master at Dunheved College, Launceston, 1913–1915. Since Jan., 1916, at H.M. Factory; Chemist-in-charge of Nitroglycerine and Cordite Paste Sections. (*Signed by*) Walter R. Moore, A. J. Leigh, E. Vanstone, Edgar Lewis, E. J. Amies.

HUGHES, WILLIAM, 63, Goldington Avenue, Bedford. Schoolmaster. Paper published, Appleby and Hughes, "The Vapour Pressures of some saturated Aqueous Solutions" (T., 1915, 1798). Teacher of Chemistry in Bedford Modern School. (*Signed by*) W. H. Perkin, A. F. Walden, N. V. Sidgwick, F. D. Chattaway, J. E. Marsh, T. V. Barker, D. L. Chapman.

HULTON, HENRY FRANCIS EVERARD, F.I.C. (by examination), 15, Oakhill Court, East Putney, S.W.15. Part author of: "Behaviour of Wheaten Flour towards Baker's and Brewer's Yeast" (*J. Soc. Chem. Ind.*, 1908 and 1909); "Toxins in Cereals" (*J. Soc. Chem. Ind.*, 1909; *J. Inst. of*

Brewing, 1910); "Estimation of Lactose" (*Analyst*, 1910); "A Study of Organisms causing 'Ropiness' in Beer and Wort"; "Action of Diastase on Starch Granules" (*Trans. Chem. Soc.*, 1914); "Estimation of Pentose and Pentosans" (*Analyst*, 1916); "An Enzyme Hydrolysing Furfuroids in Barley" (*Trans. Chem. Soc.*, 1917). For the past thirteen years Second Chemist to Watney, Combe, Reid and Co. (*Signed by*) Arthur R. Ling, Horace T. Brown, G. T. Morgan, Arthur Harden, Julian L. Baker.

ILLINGWORTH, STEWART ROY, Fern Villa, Chesham Bois, Bucks. Chemical Technologist. A.R.C.Sc.; B.Sc.(Hons., London); A.I.C. I have held the following posts: Demonstrator, Bradford Technical College (3 years); Chemist, C.I.W. Dept., Royal Arsenal, Woolwich; Chemist, Gas Lighting Improvement Co., Ltd. (5 years); Demonstrator, Battersea Polytechnic; Lieut., A.O.D.; etc. Original work: "Turpentine Substitutes" (*Proc. Paint and Varnish Soc.*); "Origin of Petroleum" (*Mining Magazine*); "Removal of CS_2 from Benzol, etc.," Brit. Patent; "The Co-operation of Science and Industry," Chas. Griffin and Sons. (*Signed by*) Oliver Trigger, M. O. Forster, Walter M. Gardner, Barker North, John Wilson, J. L. White.

ISLIP, HAROLD THOMAS, "Stilton," St. Mark's Road, Maidenhead. Analytical Chemist. Chemical student for three years at Finsbury Technical College, London, sessions 1911–12 to 1912–13. Twelve months in charge of one of Mexican Eagle Oil Co.'s laboratories. Associate of the Institute of Chemistry. (*Signed by*) Thos. McLachlan, G. T. Morgan, Arthur J. Hale, *F. Henry Streatfeild, Percy Edgerton.*

JOHNSON, GEORGE, 4, Birch Grove, Weaste, Manchester. Chemist to Messrs. Isaac Bentley and Co., Ltd., Manchester. Engaged in research work, analysis, and supervision of manufacture of Oils, Fats, Soaps, Paints, and Lubricants, and controlling and supervising the production of Glycerine. Been engaged in laboratory with above firm for 15 years, and desire to keep in touch with modern research and analytical work. (*Signed by*) B. Prentice, E. Clark, C. H. Martin, E. Green, *J. R. Appleyard.*

JUNG, JULIUS, 14, Bancroft Road, E.1. Student of Chemistry. City and Guilds Technical College, Finsbury, E.C.2. Desirous of being in constant touch with chemical literature, especially the latest. (*Signed by*) G. T. Morgan, A. J. Hale, Percy Edgerton, A. W. H. Upton, William H. Prince.

LLEWELLYN, BENJAMIN, M.Sc., 11, St. Silas Street, Ardwick, Manchester. (1) Present: Lieut. and Inspecting Ordnance Officer, Army Ordnance Department. (2) Civil: Senior Science Master and First Assistant, Secondary School, Slough, Bucks; Master of Science, Manchester University (Chemistry); Lieutenant, Army Ordnance Department; Inspecting Ordnance Officer, inspecting, proving, and testing ammunition. (*Signed by*) Harold B. Dixon, W. H. Perkin, E. Hope, W. R. Hodgkinson, Norman Smith.

MAKOVER, NATHANIEL, 13, Bancroft Road, London, E.1. Science Master, Secondary School, teaching Chemistry. B.Sc., London Internal; Associate, King's College, London. (*Signed by*) Herbert Jackson, L. E. Hinkel, M. Cutner, Patrick H. Kirkaldy, W. Crabb.

MASSON, ROBERT DUNCAN, 13, Westbourne Grove, West Kirby, Cheshire. Technical Chemist. Fellow of the Institute of Chemistry; for 12 years Chief Assistant to Mr. J. Falconer King, F.I.C., late City Analyst for Edinburgh; at present, and for the past 10 years, Chief Chemist to R. Silcock and Sons, Ltd., Liverpool, seed crushers, oil refiners, and cattle cake manufacturers. (*Signed by*) G. H. Gemmell, John S. Ford, John M. Guthrie, E. Richards Bolton, Cecil Revis.

MONTAGU, WILLIAM ALEXANDER, Lieut., 15th Battn. Highland Light Infan-

try, 7, Garturk Street, Crosshill, Glasgow. Lecturer and Instructor in Gas Warfare, employed under Scottish Command as assistant Area Gas Officer, Edinburgh. "Notes on Construction, Use, and Tactics of Chemical Grenades and Bombs," communicated and registered by War Office and Minister of Munitions; "Methods of Testing the Chemical Efficiency of Army 'Respirators'"; "The Action of Chemical Reagents on Sewage," in conjunction with Dr. Ellis, D.Sc., Ph.D.(Glasgow). Under supervision of Professor Berry, Glasgow, "Notes on the Reversion of Superphosphates when placed in Contact with Soil, Chalk, Basic Slag, etc." (*Signed by*) R. A. Berry, James McCutcheon, A. Archibald Boon, *G. G. Henderson, Thomas Gray.*

MOORE, GEORGE TURPIN, 19, Neale Street, Roker, Sunderland. Science Master. B.Sc. Degree of Durham University; two years engaged in teaching chemistry; four years' research work at Sunderland Technical College. (*Signed by*) P. Phillips Bedson, J. A. Smythe, Sydney Dunstan, C. F. Baker, *F. Gilderdale.*

NEWBERY, GEORGE, "Glenmore," Balcombe, Sussex. Works Research Chemist. Bachelor of Science, London University; Associate of the Royal College of Science, London, and Member of the Imperial College of Science and Technology, London; Research Chemist with Messrs. May and Baker, Ltd., London. (*Signed by*) H. B. Baker, James C. Philip, A. T. King, H. F. Harwood, P. W. Robertson.

PECK, WILLIAM CHARLES, 20, Bassano Street, East Dulwich, S.E.22. Analytical Chemist. Inter. Science (Internal), London; with further two years' training as an internal student of London University (Battersea Polytechnic and South-Western Polytechnic). Since 1915, chemist, Burgoyne, Burbidges and Co., Ltd., manufacturing chemists, East Ham. (*Signed by*) John Wilson, J. L. White, Thos. Farries, R. G. Halstead, William C. Harris, J. Hart-Smith, J. C. Crocker.

SCRAGG, HAROLD, Post Office, St. Anthony's, Newcastle-on-Tyne. Works Manager, Locke, Blackett and Co., Ltd., lead manufacturers, Newcastle-on-Tyne. Chief Assistant Chemist (2 years) to the Aluminium Corporation, Ltd. Undertook investigation work governing electrode manufacture. Chief Chemist and Assayer to Locke, Blackett and Co., Ltd., Newcastle-on-Tyne (2 years). Made special study of factors determining production of high-class chemical lead and lead compounds. (*Signed by*) F. G. Henderson, J. A. Smythe, J. T. Dunn, *P. Phillips Bedson, Frederick N. Binks.*

SINGER, HARRY, 147, Upper Clapton Road, London, E.5. Third year chemical student at the City and Guilds of London Institute, Technical College, Finsbury. In order to keep in touch with the latest advancements made in chemistry, both technical and theoretical, and to make use of the Chemical Society's library to aid my work at the above college. (*Signed by*) G. T. Morgan, Percy Edgerton, William H. Prince, A. Lionel Landau, Arthur J. Hale.

SMITH, ARTHUR NUTTER, 47, North Road, W. Bridgford, Nottingham. Works Chemist (drugs). Departmental Manager, Messrs. Boots Laboratories, Nottingham. Demonstrator and Assistant, Chemical Department, Technical School, Blackburn, 1902–3. Pharmaceutical Chemist (major qualification). (*Signed by*) Bertram A. Bull, H. Droop Richmond, M. Barrowcliff, Francis H. Carr, Robert H. Pickard.

SMITH, MAURICE, J.P., c/o Messrs. Cuxson, Gerrard and Co., Ltd., Oldbury. Manufacturing Chemist and Surgical Dressing Manufacturer. Manager and Technologist of Surgical Dressing and Manufacturing Chemists

Works; Major Diploma of the Pharmaceutical Society; Fellow of the Worshipful Company of Spectaclemakers. (*Signed by*) A. E. Coverdale, Geo. A. Turner, H. J. Aubrey, H. E. Hadley, H. Fox White.

SPENCE, DAVID DRYDEN, "Risca," Woodbine Avenue, Gosforth, Northumberland. Works Chemist, Messrs. The Richardson Printing Ink Co., Ltd., Team Valley Works, Gateshead. (1) Six years in secondary school, obtaining a constant foundation in (*a*) chemistry and physics, (*b*) mathematics. (2) Obtained Cambridge Local Examination Certificates (*a*) languages, (*b*) science and art (including theory and practice of chemistry). (3) Three years' study at Rutherford Technical College: (*a*) pure mathematics, (*b*) French, (*c*) physics, (*d*) organic chemistry, (*e*) inorganic chemistry, stages 1, 2, 3 (hons.). Certificate at above College under Board of Education, with distinction in the practice of chemistry. (4) Three years apprenticed Analytical Chemist. (5) Now Works Chemist, engaged in general analysis of oils, colours, fats, varnishes, and the process of manufacture of same. (6) Have done research in connexion with the furtherance of manufacture of goods in this trade hitherto placed on the market by German companies; examples, (*a*) patent driers, (*b*) varnishes. (7) Elected member of the Society of Chemical Industry. (8) Being desirous to obtain, in furtherance of my profession of chemistry, a more complete idea as to the improvements therewith connected. (*Signed by*) Frederick N. Binks, F. G. Henderson, Arthur Payne, *John H. Cheeseright, Robert McClumpha, Frederick Gilderdale.*

TAYLOR, JOHN HENRY, 54, Highbury, Newcastle-on-Tyne. Brewery Chemist. Passed qualifying examination of Pharmaceutical Society. Chief Chemist in Brewery of Bell and Taylor, Alloa (Bass Crest Brewery). Wishful to obtain the Society's publications with a view to keeping in touch with modern chemical science. (*Signed by*) F. Gilderdale, Thomas Maben, Herbert T. Platt, G. F. Merson, *Sydney Dunstan.*

TELFER, STEPHEN VEITCH, 533, Victoria Road, Crosshill, Glasgow. Captain R.A.M.C., Officer-in-Charge of Base Hygiene Laboratory, B.E.F., France; M.B., Ch.B., University of Glasgow (1910); Assistant Analyst, Messrs. Tatlock and Thomson, City Analysts, Glasgow, 1900–1904. Reports to Medical Research Committee, 1916, "Contribution to the Biochemistry of Pathogenic Anaerobes." (*Signed by*) R. R. Tatlock, R. T. Thomson, Alex. W. McLaren, *Wm. Rintoul, Edward Wheeler, N. Picton.*

THOMSON, ALEXANDER LYLE, 11, Beresford Gardens, Trinity, Edinburgh. Works Chemist. Student for three years (day classes), 1897–1900, at Royal Technical College, Glasgow, under Professor Henderson, D.Sc., M.A., F.I.C. For half-session 1900–1901 Lecture Assistant to Prof. Gray, D.Sc., Ph.D. (Evening Classes). For seventeen years (1901–1918) Works Chemist with A. B. Fleming and Co., Ltd., Caroline Park, Edinburgh, doing analytical work and manufacturing in colours, printing inks, varnishes, etc. (*Signed by*) G. G. Henderson, Thomas Gray, F. J. Wilson, *Cecil H. Desch, T. S. Patterson.*

TUCKER, THOMAS, 2, York Villas, Queen's Road, Buckhurst Hill. Association as Managing Secretary and lately General Manager for Messrs. T. Tyrer and Co., Manufacturing Chemists, for the past twenty-eight years. (*Signed by*) J. E. Coates, Sidney A. Brazier, T. Slater Price, H. D. K. Drew, H. C. Cocks.

TYRRELL, AUGUSTUS JAMES, 11, Holdenhurst Road, Bournemouth. Assistant in Chemical Department, Bournemouth Municipal College. Science Student at Bournemouth Municipal College since 1912. At present Science Lecturer's Assistant (since 1915) and Student in Water Analysis. Recently

1st Assistant Chemist to Bournemouth Gas and Water Co. (*Signed by*) Hubert Painter, Philip G. G. Moon, William George Sewell, *F. Mollwo Perkin, Robert N. Lennox.*

UPTON, WILLIAM EDWIN, 663, Leigh Road, Leigh, Lancs. Senior Science Master, Leigh Grammar School; Head of Chemical Department, Leigh Technical School. M.A. (Cantab.); B.A., Natural Sciences Tripos, 1905; late Sizar of Sidney Sussex College, Cambridge; Associate of University College, Nottingham, 1902 (1898–1902); holder of University College Free Studentship; Chemistry Master, Wheelwright Grammar School, Dewsbury, January, 1905, to July, 1907; Senior Science Master, Kilburn Grammar School, London, N.W.; and Head of Science Department, Willesden Polytechnic, N.W. (1907–1910. At Leigh since 1910. (*Signed by*) W. H. Leek, W. C. Smith, Tom R. Greenough, Harold B. Dixon, R. M. Caven, F. Stanley Kipping.

VOSS, WALTER ARTHUR, "Fairlight Glen," Eastwood Road, Rayleigh, Essex. Third Year Chemical Student at the City and Guilds of London Institute Technical College, Finsbury. To attend the Society's meetings and follow the advance in Chemistry, and to use the Society's Library. (*Signed by*) G. T. Morgan, Arthur J. Hale, A. W. H. Upton, Percy Edgerton, *R. Brightman.*

WALLACE, THOMAS, 307, Beaconsfield Street, Newcastle-on-Tyne. Assistant Chemist, Castner-Kellner Alkali Co., Wallsend-on-Tyne. 1st Class Hons., B.Sc. (Dunelm), 1915; M.Sc., 1917; Temporary Analyst, Government Laboratory, November, 1915–January, 1916; Works Chemist, Dunstan Zinc Works, January, 1916–July, 1916; Assistant Chemist (superintending laboratory work of assistants' research work under direction of Chief Chemist), Castner-Kellner Alkali Co., Wallsend, from July, 1916. (*Signed by*) Alexander Fleck, P. Phillips Bedson, J. A. Smythe, Thos. Ewan, *J. H. Young, Thomas Napier.*

WARNES, ARTHUR ROBERT, 47, Cranbrook Avenue, Cottingham Road, Hull. Works, Research, and Technical Chemist; Chemical Engineer. Nineteen years as Works Chemist, Research Chemist, Technical Chemist, Bacteriologist, and Chemical Engineer; nine months as Demonstrator and Research Chemist for Dr. F. M. Perkin, F.I.C. Original Papers: "Corrosion of Industrial Ironwork," before Society of Chemical Industry; "Investigations on Coal Tar and some of its Products" and "Coal Tar Distillation," before Midland Junior Gas Association. Publications: "Coal Tar Distillation," "Coal Tar"; thirty-four articles published in the technical press, some of which contain original matter. Teacher at Hull Technical College (evening classes); lectured on "Oils, Fats, and Waxes and Candle Manufacture," also on "Soap Manufacture," sessions 1912–13 and 1913–14; am a registered Teacher under the City and Guilds of London Institute. I hold the Bronze Medal of the City and Guilds of London Institute for soap-making; won 1st Prize in "Steam," 1906 (Hull Technical College); have carried out much original work at my places of employment, and for some time after the opening of the V.A.D. Hospital in the city (Hull) acted as Pathologist. Member of the Society of Chemical Industry; Member of the Faraday Society; Fellow of the Royal Society of Arts. (*Signed by*) Arnold R. Tankard, Harry Thompson, E. B. Atkinson, T. Luxton, Thos. A. Nightscales.

WATSON, HERBERT JOHN, 64, Peel House Lane, Widnes. Metallurgical Chemist, Messrs. James H. Dennis and Co., Ltd., Cornubia Works, Widnes, 1905–18. Papers: "Examination of Methods for Estimating Total Acidity

in Acid Chamber Escapes," Society of Chemical Industry, 1903; "Notes on Glue and Glue Testing," Society of Chemical Industry, 1904, "Notes on Benzine or Petroleum Spirit," Society of Chemical Industry, 1904; "Notes on Foaming Glue," Society of Chemical Industry, 1905. Teacher of Metallurgy (evening classes), Technical Schools, Widnes, 1912–17. (*Signed by*) John W. Towers, G. J. Warner, A. J. Squires, J. H. Naylor, H. E. Brothers.

WEBB, HARRY WILLIAM, 29, South Road, Smethwick, near Birmingham. Research Chemist. M.Sc., Birmingham; B.Sc. (1st Class Honours); A.I.C.; 1851 Exhib., 1914; four years Birmingham University; three years H.M. Factory in Works and Research Departments; at present Head, Research Department, H.M. Factory. (*Signed by*) Percy F. Frankland, Frederick Challenger, Thos. A. Smith, H. E. Smith, *Adrian J. Brown*, *A. Parker*.

WOOD, JAMES, c/o Research Department, C.W.S., 109, Corporation Street, Manchester. Analytical Chemist. M.A., B.Sc., F.I.C.; late Carnegie Research Scholar in Chemistry, University of Aberdeen; in conjunction with Emeritus Professor Japp have published Papers in the *Transactions* of the Chemical Society; late Chief Assistant in the Public Analyst's Laboratory of the Lancashire County Council; late Lecturer in Chemistry, Holt Technical School, Birkenhead; at present Chief Assistant in the Research Department of the Co-operative Wholesale Society, Manchester. (*Signed by*) Geoffrey Martin, George Tate, Alex. Caruth, *W. C. McC. Lewis*, *Alfred Holt*.

WORTH, HENRY, 70, Vyner Street, York. Teacher (Chemistry). I studied for two years (1894–5 and 1895–6) at Leeds University, taking the Intermediate and Final Science Courses, and have since been engaged in Science Teaching over four years at Rastrick Grammar School, Brighouse, and for the last seventeen years as Chemistry Teacher at Archbishop Holgate's Grammar School, York. (*Signed by*) Arthur Smithells, J. B. Cohen, H. T. Calvert, E. Norman Langham, C. E. L. Livesey, *B. V. Storr*.

The following Certificates have been authorised by the Council under Bye-Law I (3):—

DAS, GOVINDA CHANDRA, B.Sc., 20, Sunker Ghose Lane, Calcutta. Chemist. Chemist of Analytical and Research Laboratory of Explosives, Ammunition Factory, Dum Dum. (*Signed by*) B. C. Dutt, *John Watt*, *Chuni Lal Bose*.

HALE, WILLIAM JAY, University of Michigan, Ann Arbor, Mich. Associate Professor of Chemistry. Author of various books, and numerous scientific papers embodying original research in Organic Chemistry. (*Signed by*) Marston Taylor Bogert, Frederick B. Power, Ira Remsen, Chas. Baskerville.

WARBURTON, STANLEY, Titaghur Paper Mills Co., Ltd., Titaghur, India, E.B. Rly. Works Chemist. My reasons for wishing to become associated with the Chemical Society are: Being a member of the Society of Chemical Industry; being interested in Industrial Chemistry the Society Journal would be valuable. (*Signed by*) R .V. Briggs, *Puran Singh*, *M. J. Gajjar*.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, May 2nd, 1918, at 8 p.m., Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

The PRESIDENT announced that the Society has lost, through death, the following Fellows:

	Elected.	Died.
William Henry Blake	May 15th, 1890.	May 19th, 1916.
Herbert William Mills Willett	Feb. 15th, 1906.	May 9th, 1917.

Mr. A. W. Willis was formally admitted a Fellow of the Chemical Society.

Certificates for election were read for the first time in favour of:

William Baird, 16, Kinnoull Mansions, Clapton, E.5.
George Rowland Bolsover, Assoc. Met., 31, Rossington Road, Brocco Bank, Sheffield.
John William Cobb, East Garth, Lower Wortley, Leeds.
George William Dunster, 43, Wards Road, Seven Kings, Ilford.
Stanley Elliott, B.Sc., 40, Arundel Gardens, W.11.
Robert Ellison, 19, Longdin Street, Latchford, Warrington.
Frank Scott Fowweather, M.Sc., 62, Dale Street, Liverpool.
Stanley Joseph Green, B.A., Lieut. R.N.V.R., Royal Naval Air Station, Stratford, E.15.
Francis John McConnell, Anti-Gas Department, University College, Gower Street, W.C.1.

Messrs. A. J. Chapman and P. Edgerton were elected Scrutators,

and a ballot for the election of Fellows was held. The following were subsequently declared duly elected as Fellows:

George Edwin Anderson, B.Sc.
Thomas Thompson Best, Ph.D.
Rudolf Isaac Blackburn, B.A., B.Sc.
James Booth.
Cyril Bride, B.A., B.Sc.
Wilfrid John Brizell.
Giuseppe Bruni.
Colin Campbell, M.Sc.
Albert Henry Clark, Ph.G., B.Sc.
John George Clarke, M.A.
Govinda Chandra Das, B.Sc.
James Scott Dick, B.Sc.
Stanley Dixon, M.Sc.
Frederick Charles Duggleby.
Francis John Dymond, B.Sc.
Owen Charles Edwards, B.Sc.
Horace George Evans, B.A., B.Sc.
John Henry Freeman.
Charles Eddie Gallagher.
Arthur Geake, M.Sc.
Archibald Edwin Goddard, B.Sc.
Thomas Greetham.
William Jay Hale
Robert John Hughes, B.Sc.
William Hughes.
Henry Francis Everard Hulton.
Stewart Roy Illingworth, B.Sc.
Harold Thomas Islip.
George Johnson.
Benjamin Llewellyn, M.Sc.
Nathaniel Makover, B.Sc.
Robert Duncan Masson.
William Alexander Montagu.
George Turpin Moore, B.Sc.
George Newbery, B.Sc.
William Charles Peck.
Harold Scragg.
Harry Singer.
Arthur Nutter Smith.
Maurice Smith.
David Dryden Spence.
John Henry Taylor.
Stephen Veitch Telfer, M.B., Ch.B.
Alexander Lyle Thomson.
Thomas Tucker.
Augustus James Tyrrell.
William Edwin Upton, M.A.
Walter Arthur Voss.
Thomas Wallace, M.Sc.
Stanley Warburton.
Arthur Robert Warnes.
Herbert John Watson.
Harry William Webb, M.Sc.
James Wood, M.A., B.Sc.
Henry Worth.

The following paper was read:

"Spinacene, and some of its derivatives." By A. Chaston Chapman.

Ordinary Scientific Meeting, Thursday, May 16th, 1918, at 8 p.m., Professor W. J. Pope, C.B.E., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Thomas Watson Lovibond	June 15th, 1882.	May 9th.
Sir Alexander Pedler	Feb. 4th, 1870.	May 13th.

It was announced that the Council had decided to reprint the President's Address and to circulate it among Members of the

Houses of Parliament, Educational Authorities, and others holding public appointments. The Council, wishing to enlist the aid of Fellows in the circulation of the Address, have decided to provide copies, which can be obtained by Fellows free of charge on applying to the Assistant Secretary.

Messrs. H. Singer, C. E. Gallagher, and W. A. Voss were formally admitted as Fellows of the Chemical Society.

Certificates were read for the first time in favour of:

Joseph Gauld Bearn, M.Sc., Farnborough, Hants.
Roland Lebeg Townley Clarkson, 1, Lebanon Road, Wandsworth, S.W.18.
Thomas William Derrington, 20, Alrie Avenue, New Malden, Surrey.
Sidney Fleminger 297, Amhurst Road, N.16.
Fred Henesey, B.Sc., 17, Nile Street, Liverpool.
John Bright Hoblyn, 106, Tennyson Road, Luton.
John Laurence Pitchford Hollingworth, 138, Hither Green Lane, Lewisham, S.E.13.
James Henry Lindfield, 33, Preston Road, Leytonstone, E.11.
Alfred Zygmunt Molteni, 25, Caithness Road, Brook Green, W.14.
Madyar Gopal Rau, M.A., The Presidency College, Madras.
Bertram Leonard Read, B.Sc., Cranleigh School, Surrey.
Louis Stott, 34, Elmfield Terrace, Savile Park, Halifax.
John Turnbull, 18, Wilfred Street, Derby.
Richard Henry Vernon, Ph.D., 16, Park Parade, Cambridge.

The Ordinary Scientific Meeting was then adjourned and the Informal Meeting declared open.

LECTURE.

At the Ordinary Scientific Meeting of the Society to be held on Thursday, June 6th, at 8 p.m., Dr. Horace T. Brown, F.R.S., will deliver his Lecture, entitled "The principles of diffusion; their analogies and applications."

LIST OF FELLOWS, 1918.

The List of Fellows for 1918 is now in active preparation, and in order that it may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

CAIN, JOHN CANNELL. The manufacture of intermediate products for dyes. London 1918. pp. x+263. ill. 10*s*. net. (*Recd.* 26/4/18.) From the Author.

HEFTER, GUSTAV. Technologie der Fette und Oele. Vol. III. Berlin 1910. pp. xii+1022. ill. (*Recd.* 25/4/18.)
From Mr. M. Hartogs.

MITCHELL, CHARLES AINSWORTH. Edible oils and fats. London 1918. pp. xii+160. ill. 6*s*. 6*d*. net. (*Recd.* 2/5/18.)
From the Publishers: Messrs. Longmans, Green and Co.

MORGAN, GILBERT THOMAS. Organic compounds of arsenic and antimony. London 1918. pp. xviii+376. 16s. net. (*Recd.* 26/4/18.)
From the Publishers: Messrs. Longmans, Green and Co.

PALLADIN, VLADIMIR I. Plant physiology. Edited by BURTON EDWARD LIVINGSTON. Philadelphia, 1918. pp. xxv+320. ill. $3 net. (*Recd.* 13/5/18.)
From the Publishers: Messrs. P. Blakiston's Son and Co.

PARTINGTON, JAMES RIDDICK. The alkali industry. London 1918. pp. xvi+304. ill. 7*s*. 6*d*. net. (*Recd.* 6/5/18.)
From the Publishers: Messrs. Baillière, Tindall and Cox.

II. *By Purchase.*

Cowper-Coles, Sherard. Elektrolytische Verzinkung. (Monograph. angew. Elektroch., vol. 18.) Halle a. S. 1905. pp. 38. ill.

Dakin, Henry Drysdale, and Dunham, Edward Kellogg. A handbook of antiseptics. New York 1918. pp. ix + 129. ill. 7*s*. net. (*Recd.* 30/4/18.)

Engelhart, Viktor. Hypochlorite und elektrische Bleiche. Technisch-konstruktiver Teil. (Monograph. angew. Elektroch., vol. 8.) Halle a. S. 1903. pp. 275. ill.

Ephraim, Julius. Deutsches Patenrecht für Chemiker. (Monograph. angew. Elektroch., vol. 25.) Halle a. S. 1907. pp. 608.

Ferchland, P. Die elektrochemische Industrie Deutschlands. (Monograph. angew. Elektroch., vol. 12.) Halle a. S. 1904. pp. 66. ill.

Ferchland, P., and Rehländer, P. Die elektrochemischen Deutschen Reichspatente. (Monograph. angew. Elektroch., vol. 24.) Halle a. S. pp. 230. ill.

Fitz-Gerald, Francis A. J. Carborundum. (Monograph. angew. Elektroch., vol. 13.) Halle a. S. 1904. pp. 44. ill.

—— Künstlicher Graphit. (Monograph. angew. Elektroch., vol. 15.) Halle a. S. 1904. pp. 60. ill.

Jaeger, F. M. Lectures on the principle of symmetry and its applications in all natural sciences. Amsterdam 1917. pp. xii + 333. ill. 21*s*. net. (*Recd.* 2/5/18.)

Kershaw, John B. C. Die elektrolytische Chloratindustrie. (Monograph. angew. Elektroch., vol. 19.) Halle a. S. 1905. pp. 124. ill.

Le Blanc, Max. Die Darstellung des Chroms und seiner Verbindungen mit Hilfe des elektrischen Stromes. (Monograph. angew. Elektroch., vol. 3.) Halle a. S. 1912. pp. 109.

Lorenz, Richard. Die Elektrolyse geschmolzener Salze. 3 Teile. (Monograph. angew. Elektroch., vols. 20, 21, and 22.) Halle a. S. 1905. pp. 217, 257, 322. ill.

Mason, William P. Examination of water: chemical and bacteriological. 5th edition. New York 1917. pp. vi + 186. ill. 6*s*. net. (*Recd.* 25/4/18.)

Mineral Industry, The. Its statistics, technology, and trade during 1916. Edited by G. A. Roush. Vol. 25, etc. New York 1917 + . 50*s*. net. (*Reference.*)

Minet, Adolphe. Die Gewinnung des Aluminiums und dessen Bedeutung für Handel und Industrie. (Monograph. angew. Elektroch., vol. 2.) Halle a. S. 1902. pp. 129. ill.

Monographien über angewandte Elektrochemie. Edited by Viktor Engelhardt. Vol. 2, etc. Halle a. S. 1902+.

Nissenson, H. Einrichtungen von elektrolytischen Laboratorien unter besonderer Berücksichtigung der Bedürfnisse für die Hüttenpraxis. (Monograph. angew. Elektroch., vol. 4.) Halle a. S. 1903. pp. 51. ill.

Pfanhauser, W. Die Herstellung von Metallgegenständen auf elektrolytischem Wege und die Elektrogravüre. (Monograph. angew. Elektroch., vol. 5.) Halle a. S. 1903. pp. 146. ill.

—— Die Galvanoplastik. (Monograph. angew. Elektroch., vol. 11.) pp. 138. ill.

Ulke, Titus. Die elektrolytische Raffination des Kupfers. (Monograph. angew. Elektroch., vol. 10.) pp. 152. ill.

Uslar, Manuel von, and Erlwein, Georg. Cyanid-Prozesse zur Goldgewinnung. (Monograph. angew. Elektroch., vol. 7.) Halle a. S. 1903. pp. 100. ill.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY MEETING ON THURSDAY, JUNE 20TH, 1918.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics.*

Baird, William, 16, Kinnoull Mansions, Clapton, E.5. Chief chemist, Lewis Berger and Sons, Ltd., Homerton. Three years' course of technical chemistry under Professor E. J. Mills D.Sc., F.R.S., Glasgow; three years at college, and private assistant to Dr. Mills; one-and-a-half years' experimental work for Donald's Ice-Chlorine Co., Kilwinning, N.B.; twenty-five years with Lewis Berger and Sons, Ltd., Homerton—seventeen years of which as chief chemist. (*Signed by*) Edmund J. Mills, M. J. Salter, A. E. Dunstan, F. B. Thole, *F. R. Japp.*

Barham, George Henry Rowland, 74, Kensington Avenue, Manor Park, E.12. Science master, Higher Elementary School, East Ham. Responsible master, West Square Junior Technical Institute, Southwark. Inter. B.Sc. London, 1st Class (chemistry taken). Have taken the Final B.Sc. chemistry course. Have collaborated with Dr. Dunstan, F.C.S., in research work on the viscosity of ethyl-aceto-acetates. Science master since 1910. Instructor in chemistry to Chemical Industries Course students in L.C.C. Junior Technical Institute. Am now interested in the chemistry of lubricants. Elementary School Teacher's Certificate, 1st class in both parts, 1899, being trained at Borough Road Training College, 1897-9. (*Signed by*) Charles Dorée, F. B. Thole, A. E. Dunstan, *Gerald Druce, J. C. Crocker.*

Bearn, Joseph Gauld, Farnborough. Research chemist. B.Sc. (Manches-

ter), 2nd Class Hons. in Chemistry, 1904; M.Sc. (Manchester), 1907. During the last ten years have carried out research work in connection with oils, paints, and varnishes. (*Signed by*) John O. Hughes, H. Arwel Thomas, A. U. Newton, T. W. Kirkwood, E. Mendoza, Gilbert Palmer, Bertram Campbell.

BELL, JOSEPH WILLIAM, 130, Manchester Road, Burnley, Lancs. Science teacher, Municipal Technical Institute, Burnley. Student at University College, London; took chemistry under the late Prof. Ramsay. Have been a teacher of chemistry, physics, and mathematics for the past twenty years. (*Signed by*) Raymond Ross, H. J. C. Mathews, E. B. Naylor, Jno. P. Leather, Harry Heap, *T. J. Drakeley*, *Ernest Geo. Gaul.*

BOLSOVER, GEORGE ROWLAND, 31, Rossington Road, Brocco Bank, Sheffield. Metallurgist. Assoc. Met. (Sheffield University). Carnegie Scholarship Iron and Steel Inst. (subsequently declined owing to stress of work). Pupil Yorkshire Testing Lab. Charge of laboratories Messrs. Hy. Bessemer and Co., Ltd. Present—Brown Firth Research Laboratories. (*Signed by*) J. E. Stead, W. E. S. Turner, W. P. Wynne, John Evans, Jas. T. Stevenson.

BROMLEY, HENRY ALDOUS, The Willow, Cambridge Road, W. Wimbledon, S.W.19. Crown servant. Expert in the chemistry of paper to H.M. Stationery Office. Lecturer on the chemistry of paper to the London County Council. A process for the recognition of gelatine in presence of starch (*Paper Maker*, March, 1914). Author of "Outlines of Stationery Testing" (Griffin, 1913), and of original research into the colouring matters used for paper-making fibres (*Paper Maker*, February, 1914). A process for the estimation of tar acids in paper (*Paper Maker*, September, 1914). (*Signed by*) R. W. Sindall, Henry P. Stevens, Edward Bevan, C. F. Cross, *J. William Bacon.*

CASHMORE, ALBERT ERIC, 32, Vicarage Road, Smethwick, Birmingham. Process chemist, H.M. Factory (T.N.T. Dept.). Student at Birmingham University during sessions 1912–1913, 1913–1914; have passed intermediate examination, and completed second year, taking chemistry as principal subject; released from Army, March, 1917, and have since been engaged as above. (*Signed by*) Percy F. Frankland, Frederick Challenger, H. A. Scarborough, A. Parker, F. H. Garner, C. E. Wood.

CLARKSON, ROLAND LEBEG TOWNLEY, 1, Lebanon Road, Wandsworth, London, S.W.18. Analytical works chemist. Chemist to the Burgh Castle Cement Works, 1914; second chemist of the Harty Factory of the Cotton Powder Co., Ltd., 1916–1917. Now at Wandsworth, and desirous of being able to attend the Society's meetings. (*Signed by*) C. S. Garland, O. Silberrad, John Hughes, *J. H. Coste*, *C. S. Graham.*

COBB, JOHN WILLIAM, East Garth, Lower Wortley, Leeds. Livesey Professor Coal Gas and Fuel Industries, The University, Leeds. "Thermal Study of the Carbonisation Process," *J.C.S.*, 1915; "Synthesis of a Silicate" (six papers), *J.S.C.I.*, 1910, and others mainly technical. (*Signed by*) Arthur Smithells, H. M. Dawson, J. B. Cohen, H. J. Hodsman, S. F. Dufton.

DAILEY, HUBERT WILLIAM, 19, Beverley Road, Anerley, Kent. Stores Department, Port of London Authority. Student of applied chemistry at Battersea Polytechnic and Sir John Cass' Institute; City and Guilds Examinations; oils and fats, bronze medal; iron and steel manufacture, 1st class certificate in Advanced and Honours Grades. (*Signed by*) J. Wilson, D. R. Davey, J. L. White, F. M. Thomas, *J. H. Johnston.*

DERRINGTON, THOMAS WILLIAM, 20, Alric Avenue, New Malden, Surrey.

Analytical chemist. Analyst to the L. and S.W. Ry. Co. for twenty-three years; assistant demonstrator to Prof. A. Humboldt Sexton at Glasgow and West of Scotland Technical College; science master at Stafford Grammar School. (*Signed by*) Harold G. Colman, John H. B. Jenkins, L. Archbutt, Chas. J. P. Fuller, W. R. Bird, H. Gripper.

Dunster, George William, Northdene, 43, Wards Road, Seven Kings, Essex. Technical chemist to firm of oil refiners, colour makers, and paint varnish manufacturers. Twenty years as technical chemist and works manager, etc., to Gross, Sherwood, and Heald, Ltd.; assistant lecturer and demonstrator in oils, paints, and colours at Borough Polytechnic, London, S.E. For use of Library. (*Signed by*) Hubert R. Wood, C. E. Cooke, R. S. Morrell, W. G. Aston, George Dean, F. Henry Streatfeild.

Edge, Arthur Broughton, Tudor House, Maidenhead, Berks. Lieut., R.A. Now engaged in chemical research work under the Ministry of Munitions; his course in chemistry was not completed owing to the outbreak of war; he wishes to keep in touch with recent developments in chemistry, especially in its relations to mineralogy. (*Signed by*) Jocelyn Thorpe, Kenneth C. D. Hickman, J. N. E. Day, H. B. Baker, James C. Philip.

Elliott, Stanley, 40, Arundel Gardens, W.11. Analytical chemist (Army at present). B.Sc. (Hons. Chem.) Lond.; F.I.C. (*Signed by*) Cecil H. Cribb, R. H. A. Plimmer, Guy T. P. Tatham, Herbert Jackson, Patrick H. Kirkaldy, L. E. Hinkel.

Ellison, Robert, 19, Longdin Street, Latchford, Nr. Warrington. Analytical and technical chemist. Certified lecturer on alkali manufacture. Bronze medallist, C. and G. of London Inst., for alkali manufacture, 1914–1915; bronze medallist, C. and G. of London Inst., for soap manufacture, 1916–1917; Fellow of American Chemical Society; final certificates (Board of Education) in inorganic, physical, and organic chemistry; researches on hydrogen and water gas, etc. (*Signed by*) E. F. Armstrong, S. J. Peachey, Chas. W. Moore, John Allan, T. P. Hilditch, *Jas. Grant, A. G. Green.*

Fitzgerald, Francis William, 128, Earlham Grove, Forest Gate, E. Chemical manufacturer (trading as Senior, Crozier and Co., Union Works, Stratford, E.). Sole proprietor and works chemist of the above business, producing fine and heavy chemicals; studied chemistry at the West Ham Technical Institute; have also worked in the laboratories of several London manufacturing chemists. Am desirous of becoming a Fellow of the Chemical Society in order to have the use of its Library and the Society's Journal. (*Signed by*) Francis A. B. Jewson, E. Geo. Streimer, W. A. Wayland, *Maurice White, Ernest S. Spencer, Thomas W. Morson, Percy K. Le May.*

Fleminger, Sidney, 297 Amhurst Road, N.16. Analytical chemist. For the last twelve years assistant to Dr. Frank L. Teed, public analyst; gas examiner to the London County Council since 1907; five years in the laboratories of the St. George's Hospital Medical School; two years as demonstrator in chemistry. (*Signed by*) Frank L. Teed, William H. Prince, H. Mansfield, Charles A. Keane, Harry Singer.

Fowweather, Frank Scott, 62, Dale Street, Liverpool. Analytical, consulting, and technical research chemist. B.Sc., 1st Class Honours in chemistry (Liverpool University), 1914; M.Sc., 1915; "Isaac Roberts" scholar and "Willox" exhibitioner, Liverpool University; Associate of Institute of Chemistry; formerly works chemist with Messrs. Evans, Sons, Lescher, and Webb, Runcorn; later research chemist with British Dyes, Ltd., Huddersfield; now junior partner in firm of Ormerod and Fowweather, analytical and consulting

chemists, Liverpool. (*Signed by*) N. G. Stevenson Coppin, W. C. McC. Lewis, T. M. Nightingale, C. A. Fogg, Ernest Boardman.

GREEN, STANLEY JOSEPH, Stratford, London, E. Lieutenant, R.N.V.R., attached to Royal Naval Air Service for chemical work. First Class Honours in Natural Science Tripos, Cambridge, 1910; in charge of chemical work (research, and work connected with manufacturing plant) at R.N. Air Station. (*Signed by*) T. Slater Price, George Senter, William J. Pope, H. C. Greenwood, Sidney A. Brazier, H. D. K. Drew, *J. Newton Friend.*

GUPTA, NALINI MOHAN, Panposh, B.N. Ry., India. Chemist, Bisra Stone Lime Co., Ltd. (managing agents, Messrs. Bird and Co., Calcutta). M.Sc., Calcutta; Associate of Indian Institute of Science, Bangalore; author of "Lead Cyanide," *Proceedings*, Chemical Society, 1913, Vol. 29; "Borohydrates," with Dr. Travers and Roy, *Journal* of the Indian Institute of Science, Bangalore, Vol. I., Part I.; late demonstrator in general chemistry, Indian Institute of Science, Bangalore; chemist to the Calcutta Sewage Disposal Experimental Works (1914–1917); at present chemist to Messrs. Bird and Co., Calcutta, studying the chemistry and manufacture of Portland cement. (*Signed by*) Morris W. Travers, J. J. Sudborough, H. E. Watson, P. Bruhl, P. C. Rây.

HARTUNG, ERNST JOHANNES, 9, Glendearg Grove, Malvern, Melbourne, Australia. M.Sc. Acting lecturer on chemistry, University of Melbourne. Author of the following papers:—"A New Method for Determining the Specific Heats of Liquids," *Transactions* of Faraday Society, Vol. 11, Part I., 1915. "A Contribution to the Theory of Solution," *Trans.* of Faraday Society, Vol. 12, Part I., 1916. "The Reaction between Aniline and Carbon Tetrachloride" (submitted recently to the Chemical Society). (In conjunction with Dr. A. C. D. Rivett), "An Occurrence of Ammonium Chloride," at Frankston, Vic. *Proc.* Roy. Soc. Vic., Vol. 28, p. 133. (*Signed by*) Orme Masson, Heber Green, A. C. D. Rivett, *Irvine Masson, N. V. Sidgwick.*

HENESEY, FRED, 17, Nile Street, Liverpool (at present at Anti-gas Department). Analytical chemist. B.Sc. Hons., University of Liverpool; assistant to Chemical Adviser, 9th Army Corps, B.E.F., France; assistant Anti-gas Department. (*Signed by*) E. C. C. Baly, H. H. Froysell, W. C. McC. Lewis, F. G. Donnan, *R. Robinson.*

HOBLYN, JOHN BRIGHT, 106, Tennyson Road, Luton, Beds. Chemist and metallurgist. Associate Royal College Science Chemistry, first class; Fellow of the Institute of Chemistry; late senior science master, Luton Modern School; chemist and metallurgist to Vauxhall Motors, Ltd. Author of paper, "Commercial Steels and their Heat Treatment," Institution Automobile Engineers, 1918; joint author, "Story of the Five Elements." (*Signed by*) James C. Philip, P. W. Robertson, M. O. Forster, William A. Tilden, *H. B. Baker.*

HOLLINGWORTH, JOHN LAURENCE PITCHFORD, 138 Hither Green Lane, Lewisham, S.E.13. Pharmacist, Victoria Hospital for Children, Tite Street, Chelsea, S.W.; Fellow of the Linnean Society; member of the Pharmaceutical Society; member of the Association of Hospital Officers. Engaged for many years in the practice of analytical chemistry and general pharmaceutical chemistry. (*Signed by*) Henry O. Huskisson, Robert W. Lindsey, J. Wicliffe Peck, *Thomas Tickle, Alex. Gunn, C. E. Corfield, Henry L. Smith.*

LINDFIELD, JAMES HENRY, 33, Preston Road, Leytonstone, E.11. Sugar

refiners' chemist. Was for five years student in chemistry at the East London College. Contributions with Prof. J. T. Hewitt: "The Nitration of the Three Tolueneazophenols." *Trans.* Chem. Society, 1901, Vol. **79**. Part author of "The Rapid and Accurate Estimation of Iron in Cane and Beet Sugar Factory Products" (*International Sugar Journal*, 1912, **14**, 428–485. Part author of "The Determination of Ash of Cane and Beet Sugar Products" (*International Sugar Journal*, 1918, **20**, 114–117. Twelve years works chemist to Messrs. Martineau's, Ltd., Whitechapel, sugar refiners. (*Signed by*) Chas. E. Eastick, James P. Ogilvie, Fred. C. Eastick, J. T. Hewitt, Arthur R. Ling.

Lockspeiser, Ben, M.A., 21 Thornby Road, Clapton, London, E.5. Technical assistant (Munitions Inventions Department). First class Natural Sciences Tripos (1912), Cambridge University; Second class Mechanical Sciences Tripos (1913), Cambridge University; late scholar and prizeman, Sidney Sussex College, Cambridge. (*Signed by*) W. J. Pope, F. G. Donnan, Henry Terrey, *H. J. H. Fenton, J. N. Collie, S. Smiles.*

McConnell, Francis John, 13, Sefton Road, Liverpool, N. Analytical chemist. Privately tutored for mathematics, physics (Oakes Institute); three years' training under (late) Edward Davies, of Liverpool, and two years as assistant to H. E. Davies, F.I.C., B.Sc., M.A.; works chemist for Cunard S.S. Co, and experience also in explosive and coal tar laboratories; also at Lever Bros., Ltd.; two years in Chemical Warfare Laboratories. (*Signed by*) E. F. Harrison, W. C. Ball, H. S. Raper, L. A. Levy, E. J. Wilson, A. G. Harrington.

Molteni, Alfred Zygmunt, 25, Caithness Road, Brook Green, W.14. Research chemist at the works of Messrs. Jenson and Nicholson, Ltd., Stratford, E., colour, varnish, and enamel manufacturers. Studied at the Imperial College of Science and Technology, London (1912–1915); Associate of the Royal College of Science (A.R.C.S.), chemistry; nearly three years' works experience, principally research in oils and aeroplane varnishes and dopes, including analytical work in allied products. (*Signed by*) H. B. Baker, James C. Philip, A. T. King, Arthur A. Eldridge, H. F. Harwood.

Newbery, Edgar, The University, Manchester. Lecturer in electrochemistry. B.Sc.(Lond.), D.Sc.(Vict.). Author of various papers on electromotive forces in alcohol, overvoltage, iron hydration, steel corrosion, etc., published in *J.C.S.*, and *Proc. Roy. Soc.* (*Signed by*) Harold B. Dixon, Arthur Lapworth, C. A. Edwards, Norman Smith, F. P. Burt, W .K. Slater.

Powell, Edward Churton, 39, Lombard Street, E.C. Chemical manufacturer. Chairman and managing director of a company manufacturing organic chemicals. (Signed by) J. C. Cain, Daniel L. Couch, W. H. Simmons, Edward L. Joseph, Harold Davies.

Madyar, Gopal Rau, The Presidency College, Madras. Madras University research student in chemistry. B.A. Honours, Chemistry, 1915; M.A., 1918; research student in chemistry, 1915–1918. Joint author of three papers published in the Chemical Society's *Transactions.* (*Signed by*) J. L. Simonsen, J. J. Sudborough, H. E. Watson, F. L. Usher, *Gilbert J. Fowler.*

Read, Bertram Leonard, Cranleigh School, Surrey. Schoolmaster. (i) B.Sc. Honours (London); (ii) Associate of the Nottingham University College; (iii) chemistry master at Cranleigh School, in charge of the chemistry department. (*Signed by*) L. Orange, R. M. Caven, F. Stanley Kipping, *Arthur Jaques, R. C. Farmer.*

Seffer, Runar Ivar Olsson-, 1, Royal Exchange Place, Calcutta. Director,

Chilean Nitrate Propaganda Office and Laboratory, Calcutta, India. Former positions: plant physiologist, Tezonapo Botanical Station and Rubber Laboratory; chief botanical section, Dept. of Agr., Mexico. Present positions: director, Chilean Nitrate Propaganda, India; chemist, Chilean Nitrate Propaganda Laboratory, Calcutta. Author of publications of Dept. of Agr., Mexico: "Rubbers and Gutta-perchas in Mexico, with Analyses"; "Microchemistry of *Argemone mexicana*"; "Collectors' and Students' Handbook." Nitrate propaganda pamphlets, etc. (*Signed by*) J. McGlashan, William S. Myers, R. V. Briggs, *Eric Hayward, G. D. Hope.*

Speedy, Alan, 81, Burges Road, East Ham, E.6. Works chemist at the India Rubber, Gutta Percha Co., Silvertown. A student of the East Ham Technical College for the past eleven years; author of "A Simple Instrument for the Determination of Viscosity," see *J. S. Chem. Ind.*, June 15th, 1915, No. 11, Vol. XXXIV. (*Signed by*) W. H. Barker, F. B. Thole, A. E. Dunstan, A. J. Harvey, R. C. Denington, Arthur R. Ling.

Stott, Louis, 34, Elmfield Terrace, Savile Park, Halifax. Research and works chemist. Advanced chemical student, Halifax Technical School; silver medallist, City and Guilds of London (twice); five years as technical chemist in England for Meister, Lucius, & Brüning (twelve months in their laboratories in Germany); at present works manager and chemist to firm of fine chemical manufacturers (phenacetin, salicylates, etc.). (*Signed by*) Clement A. Crook, J. A. Dewhirst, W. J. Stansfield, H. P. Hird, R. E. Oldroyd.

Thomas, John, Solway Dyes Co., Humell Hill Works, Carlisle. Research chemist. B.A.(Cantab.), D.Sc.(Wales); "Addition of Bromine and Unsaturated Acids," Parts I. and II. (joint author); "Isolation of the Aromatic Sulphuric Acids"; "The Four Stereoisomeric Tetrahydrodimethylquinolines"; "The Separation of Primary and Secondary Arylamines"; all published in the *Transactions* of the Society. (*Signed by*) Wm. Rintoul, Thos. J. Nolan, W. J. Pope, W. J. S. Naunton, *Alex. Findlay.*

Turnbull, John, 18, Wilfred Street, Derby. Research chemist (chief assistant to Dr. Elkind). Eleven years as assistant colourist at Turnbull and Stockdale, Ltd., calico printers, Ramsbottom; chemist to Hardman's, Ltd., tar works, Birmingham; chemist in employ of Turner Bros., Ltd., Trafford Park, Manchester; research chemist in employ of British Cellulose and Chem. Mfg. Co., Ltd., Spondon; studied chemistry (organic and inorganic) under G. M. Norman, F.I.C., B.Sc., F.C.S.; higher certificate of Board of Education in chemistry; member of Society of Chem. Industry; member of Society of Dyers and Colourists. (*Signed by*) H. H. H. Lorenz, Wm. P. Skertchly, J. F. Briggs, J. H. Jeffery, E. P. Hedley, Jos. Yates.

Vernon, Richard Henry, 16, Park Parade, Cambridge. Chemical Warfare Dept., Lieut., 3rd Dorsets. Ph.D.(Zurich). (*Signed by*) C. S. Gibson, W. J. Pope, W. H. Mills, C. T. Heycock, James C. Philip.

Whalley, Hubert Charles Siegfried de, Park House, 18, Brandram Road, Lee, S.E.13. Works and research chemist to the Micanite and Insulators Co., Ltd., Walthamstow. Internal student of London University at Goldsmiths' College, 1910–1915; Int. B.Sc., 1912; have taken the complete course for honours chem. final degree; four years assistant chemist and three years chief chemist to the Molassine Co., Ltd.; member of the Society of Public Analysts and other analytical chemists. (*Signed by*) Charles A. Keane, Henry J. S. Sand, L. J. de Whalley, Ern. W. Harvey, Hugh Main, W. P. R. Newlands.

Whyte, William, 98, Kirkmanshulme Lane, Longsight, Manchester. Chemist in charge of acid plant at Clayton Aniline Co., Ltd., Clayton, Man-

chester. One year at Technical College, Rockhampton, Queensland, studying theoretical chemistry and laboratory practice; three years at Gordon's College, Aberdeen, theoretical and practical chemistry; two years at Aberdeen University, theoretical and practical chemistry; ten months as shift chemist with Messrs. Chance and Hunt, of Oldbury, on acid plant; nineteen months as chemist in charge of plant at Clayton Aniline Co., Clayton, Manchester. (*Signed by*) W. H. Bentley, Robert Dodd, A. Potter, *E. Clark*, *W. Moore Nichols.*

WOOLLEY, SAMUEL WALTER, 58, North Hill, Highgate, N.6. Technical journalist. Pharmaceutical chemist; editor of "The Chemist and Druggist"; corresponding member of the Société Royale de Pharmacie de Bruxelles; author of "The Chemist-Optician." (*Signed by*) William Kirkby, Fred. W. Fletcher, Charles Alex. Hill, Ernest J. Parry, Edward F. Linstead, T. H. W. Idris.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 6th, 1918, at 8 p.m., Professor W. J. Pope, C.B.E., F.R.S., President, in the Chair.

It was announced that the Society has lost, through death, the following Fellows:

	Elected.	*Died.*
Walter Augustus Handcock	Dec. 6th, 1900	May 26th
Henry Tylston Hodgson	Apr. 17th, 1873	May 22nd
Mulgrave Daniel Penney	Mar. 7th, 1870	Mar. 5th

Messrs. A. Geake, K. G. Laiwala, and R. Brightman were formally admitted as Fellows of the Chemical Society.

Certificates for election were read for the first time in favour of:

Frank Bainbridge, Woodland View, West Road, Loftus-in-Cleveland.
Reginald Percy Leopold Britton, 58, The Crescent, Wimbledon Park, S.W.19.
John Edwyn Davies, B.Sc., Taimawr, Swansea Road, Merthyr Tydvil.
Campbell Falconer, the Hall, Osbaldwick, York.
Bernard Arthur James Jeffs, 35b, Gladstone Avenue, Wood Green, N.22.
Edwin Percy Keeble, Summer Lodge, Kenilworth.
Albert Victor Mountford, 38, Gamblins Road, St. Martins, Christchurch, New Zealand.
Frederick Gerald Tryhorn, M.Sc., 45, Hallville Road, Mossley Hill, Liverpool.
Gerald Noel White, B.Sc., 15, West End Avenue, Pinner, Middlesex.
John William Reginald Youll, "Keswick," Rainsford Avenue, Chelmsford.

Dr. Horace T. Brown then delivered his lecture, entitled "The Principles of Diffusion; their Analogies and Applications." A vote of thanks to Dr. Horace T. Brown for his lecture, proposed by Professor P. F. Frankland and seconded by Professor Farmer, was carried with acclamation.

Ordinary Scientific Meeting, Thursday, June 20th, 1918, at 8 p.m., Mr. A. Chaston Chapman in the Chair.

It was stated that the following Fellows had died:

	Elected.	Died.
Thomas Farries	Dec. 1st, 1870.	June 5th.
Alexander Milne	May 7th, 1885.	May 29th.

The following announcements were made:

(1) That a communication had been received from the Committee of the Van't Hoff Fund for the endowment of research in pure and applied chemistry. The amount from this fund available for distribution during 1919 is about £150.

A Committee, consisting of Professor A. F. Holleman (President), Professor S. Hoogewerff, Professor A. Smits, and Professor E. H. Büchner (Secretary), has been appointed to award grants. Applications should be sent before November 1st, 1918, by registered post, to "Het Bestuur der Koninkklyke Akademie van Wetenschappen; bestemd voor de Commissie van het 'Van't Hoff-fonds' Trippenhuis, Kloveniersburgwal, te Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.

(2) The Council have decided to issue the List of Fellows in the near future; it will not be circulated in the usual manner, but may be procured by Fellows on applying to the Assistant Secretary.

(3) In view of the shortage of paper, the Council wish to emphasise the necessity of authors reducing as far as possible the length of scientific communications submitted to the Society.

(4) The Council have appointed a Committee, consisting of the following, Messrs. W. R. Bousfield, A. G. Green, C. A. Hill, G. T. Morgan, A. Scott, and W. P. Wynne, and the Officers, namely, Messrs. W. J. Pope, M. O. Forster, S. Smiles, J. C. Philip, and A. W. Crossley, to consider the revision of the Bye-laws. Opportunity will be afforded to Fellows for bringing forward suggestions on the matter.

Certificates of candidates for election were read for the first time in favour of:

Claud Diamond, B.Sc., 17, Moresby Road, Upper Clapton, E.5.
John Edward Doodson, Smithy Bridge, Rochdale.

John Robert Douglas, A.R.C.S.I., West-field, Saltcoats, B.O., Ayrshire.
Laurence Francis Le Brocq, B.Sc., "Akender," Guildford Road, South Farnborough, Hants.
Donald Neil McArthur, B.Sc., 28, Grafton Street, Glasgow.
George Frederick Robertshaw, Mornay, Kearsley Road, Higher Crumpsall, Manchester.
Eric Sinkinson, 14A, Albert Bridge Road, S.W.11.
Thomas Rinck Stopford, M.Sc., "Woodbank," Macclesfield.

Certificates for election have been authorised by the Council for presentation to ballot under Bye-Law I(3) in favour of:

James Garfield Anderson, M.Sc., Southland Boys' High School, Invercargill, New Zealand.
Juan Pedige Charles Chandrasena, B.Sc., Technical Schools, Colombo, Ceylon.

Messrs. F. H. Lowe and J. Reilly were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected as Fellows.

William Baird.
George Henry Rowland Barham.
Joseph Gauld Bearn, M.Sc.
Joseph William Bell.
George Rowland Bolsover.
Henry Aldous Bromley.
Albert Eric Cashmore.
Roland Lebeg Townley Clarkson.
John William Cobb.
Hubert William Dailey.
Thomas William Derrington.
George William Dunster.
Arthur Broughton Edge.
Stanley Elliott, B.Sc.
Robert Ellison.
Francis William Fitzgerald.
Sidney Fleminger.
Frank Scott Fowweather, M.Sc.
Stanley Joseph Green, B.A.
Nalini Mohan Gupta, M.Sc.
Ernst Johannes Hartung, M.Sc.
Fred Henesey, B.Sc.
John Bright Hoblyn.
John Laurence Pitchford Hollingworth.
James Henry Lindfield.
Ben Lockspeiser, M.A.
Francis John McConnell.
Alfred Zygmunt Molteni.
Edgar Newbery, D.Sc.
Edward Churton Powell.
Madyar Gopal Rau, M.A.
Bertram Leonard Read, B.Sc.
Runar Ivar Olsson Seffer.
Alan Speedy.
Louis Stott.
John Thomas, B.A., D.Sc.
John Turnbull.
Richard Henry Vernon, Ph.D.
Hubert Charles Siegfried de Whalley.
William Whyte.
Samuel Walter Woolley.

The following papers were read:

"The equilibrium isotherm of association in organic solutions the solvent of which is unassociated as pure liquid." By W. R. Innes.

"Diazoimides of nitro- and 2:6-dichloro-p-phenylenediamine." By G. T. Morgan and D. A. Cleage.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Dubosc, A., and Luttringer, A. Rubber: its production, chemistry and synthesis in the light of recent research. A practical handbook for the use of rubber cultivators, chemists, economists and others. English edition by Edward W. Lewis. London 1918. pp. xi+383. ill. 21*s*. net. (*Recd.* 6/6/18.)
From the Publishers: Messrs. Charles Griffin.

Plimmer, Robert Henry Aders. Practical organic and bio-chemistry. New and revised edition. London 1918. pp. xii+636. ill. 18*s*. net. (*Recd.* 3/6/18.)
From the Publishers: Messrs. Longmans, Green and Co.

Ramsay, Sir William. See Tilden, Sir William A.

Tilden, Sir William A. Sir William Ramsay, K.C.B., F.R.S. Memorials of his life and work. London 1918. pp. xvi+311. ill. 10*s*. net. (*Recd.* 6/6/18.) From the Author.

Young, Sydney. Stoichiometry. 2nd edition. London 1918. pp. xiv+363. ill. 12*s*. 6*d*. net. (*Recd.* 4/6/18.)
From the Publishers: Messrs. Longmans, Green and Co.

II. *By Purchase.*

Browning, Carl Hamilton. Applied bacteriology. Studies and reviews of some present-day problems. London 1918. pp. xiii+291. ill. 7*s*. 6*d*. net. (*Recd.* 12/6/18.)

Chemical Manufacturers' Directory of England, Wales and Scotland, with some of the firms in Ireland, for 1918. Being a list of the principal manufacturers of chemicals used in commerce, medicine, agriculture, and the arts. 50th edition. London 1918. pp. 235. 3*s*. 6*d*. net. (*Reference.*)

Collins, Sydney Hoare. Plant products and chemical fertilizers. London 1918. pp. xvi+236. 7*s*. 6*d*. net. (*Recd.* 12/6/18.)

PRESIDENTIAL ADDRESS.

Reprints of the President's Address delivered before the Chemical Society on March 21st will be ready in July. Those Fellows desirous of assisting the Council in the circulation of this Address are reminded that copies can be obtained from the Assistant Secretary free of charge.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, November 7th, 1918, at 8 p.m., Professor W. J. POPE, C.B.E., F.R.S., President, in the Chair.

The PRESIDENT announced that the Society had lost, through death, the following Fellows:

Died on Service.

	Elected.	Died.
Edward Frank Harrison...........	Feb. 15th, 1894.	November 4th.

James Bayne	June 14th, 1874.	
Joseph John Bowley	Feb. 20th, 1896.	August 21st.
Harry Broadbent	April 4th, 1889.	July 25th.
William Edward Callister	Dec. 2nd, 1909.	August 15th.
William Adam Dixon	Dec. 18th, 1862.	November 6th, 1917.
Charles Thomas Foreman	Dec. 5th, 1907.	October 7th.
Charles James Pemeller Fuller ...	Feb. 20th, 1896.	June 2nd.
David Smith Jardin	Feb. 19th, 1902.	May 13th.
Sydney Lupton	Dec. 5th, 1872.	July 10th.
Edward Matthey	Jan. 17th, 1874.	October 21st.
Elias Mendoza	Feb. 21st, 1918.	September 27th.
Alfred Senier	March 4th, 1875.	June 29th.
Walter Dalrymple Severn	May 7th, 1896.	August 11th.
John William Shepherd	June 15th, 1899.	July 11th.
Henry Charles Stephens	April 15th, 1880.	July 8th.
Christopher Wilson	Dec. 6th, 1894.	August 7th.

The Council desires to direct the attention of Fellows to the Army Education Scheme which has been prepared by the War

Office. Under this scheme, an appeal is made for voluntary lecturers who would be willing to deliver occasional lectures to the troops in the United Kingdom, France, or Italy. In accordance with the scheme, the lecturers will not receive fees, but all expenses will be defrayed. Fellows who contemplate taking part in the scheme are requested to communicate with the Assistant Secretary, from whom further particulars can be obtained.

Messrs. W. R. Grist, F. W. Fitzgerald, A. Z. Molteni, R. L. T. Clarkson, and W. J. Lund were formally admitted as Fellows of the Chemical Society.

Certificates were read for the first time in favour of:

Lauchlan Henry Pyke Acland, B.A., Island View, Barton-on-Sea, Hants.
Valentine George Anderson, 31 Victoria Avenue, Canterbury, Victoria, Australia.
William Learmouth Baillie, 70, Hampton Road, Clifton, Bristol.
Ernest George Balls, B.Sc., Orford House, Wellington Road, Wanstead, E. 11.
Percy Barrs, 33, Lancaster Park, Richmond Hill, Richmond, Surrey.
William Andrew Stewart Blaine, B.Sc., Ardbana Crescent, Coleraine.
John Harold Bright, 157, Greenvale Road, Eltham, S.E. 9.
Hubert Thomas Stanley Britton, B.Sc., Lynn Dene, Court Road, Kingswood, Bristol.
Charles Daniel Buckley, 52, Gilda Brook Road, Eccles.
Jules Cofman-Nicoresti, 15, Speenham Road, S.W. 9.
Maurice Copisarow, M.Sc., The University, Manchester.
Cyril Murton Croft, 37, Rusholme Road, Putney, S.W. 15.
Herbert Hector Donaldson, 15, Ash Leigh, Anfield, Liverpool.
George Zephirin Dupain, "Symington," Parramatta Road, Ashfield, Sydney, Australia.
Herbert John Evans, B.Sc., 7, Market Street, Haverfordwest.
James Foster, 59, Elizabeth Street, North Woolwich, E. 16.
Alfred Edwin Gates, 32, Conway Road, Luton.
Herbert William Gepp, Hobart, Tasmania.
Geoffrey Gladding, M.Sc., 4, Heaton Road, Heaton Norris, Stockport.
George Grant, "Tinniver," Balmoral Avenue, Cathcart, Glasgow.
John Russell Green, B.Sc., 2, Belmont Park, Lee, S.E. 13.
William Duthie Haigh, B.A., B.Sc., 15, Cavendish Avenue, Church End, Finchley, N.
Harry Hepworth, M.Sc., Nobel's Explosives Co., Stevenston.
Herbert Leslie Howard, 44, Disraeli Road, Forest Gate, E. 7.
William Claude Jago, 17, Wilbury Avenue, Hove, B.O., Brighton.
Cosmo Johns, Burngrove, Pitsmoor Road, Sheffield.
Clifford William Judd, B.Sc., 4, Maythorne, Ardrossan Road, Saltcoats, B.O., Ayrshire.
Frederick John Kettel, 47, Limes Road, Beckenham, Kent.
Thomas Kilby, 1, Westfield Road, Toller Lane, Bradford.
Norman Victor Sydney Knibbs, B.Sc., The Hostel, Langwith, Mansfield.
Ernest Alfred Littlewood, 12, Brookfield Road, Crumpsall, Manchester.

Shih Chen Loo, 70, High Lane, Chorlton-cum-Hardy, Manchester.
John Armour McKerrow, M.A., B.Sc., 2, Kymer Villas, Kidwelly, Carmarthenshire.
Charles Stewart Maries,, B.Sc., Eggesford Cottage, Queens Road, Aldershot.
Norman Louis Matthews, 45, Tyrwhitt Road, Brockley, S.E. 4.
Robert Alfred Moore, B.Sc., 9, Coniston Avenue, West Jesmond, Newcastle-on-Tyne.
William Newton, Station Road, Wootton Bassett, Swindon.
Douglas Norbury; Lyndene, Lansdowne Road, West Didsbury, Manchester.
Edwin Hart Nurse, B.Sc., "Southwold," Lewis Road, Sutton, Surrey.
Mehtab Singh Obroi, B.Sc., Gordon College, Rawal Pindi, India.
Leslie Henry Parker, M.A., D.Sc., "The Chestnuts," Church Road, Leatherhead.
John Paterson, 1, Rowallan Gardens, Glasgow.
Wilfred Stanley Pheasey, Second Corps, B.E.F.
Alexander Park Porter, 157, Greenvale Road, Eltham, S.E. 9.
Joseph Francis Pratt, 77, Hanbury Road, Pontnewynydd, Pontypool.
Ralph John Pugh, 99, Lonsdale Road, Barnes, S.W. 13.
George Thomson Purves, "Thirlestane," Chryston, Glasgow.
Dudley Ridge, 7, College Place, Brighton.
Frederick Maurice Rowe, M.Sc., 5, Woodbine Terrace, Latchford, Warrington.
Walter Salmon, 17, The Grove, Eccles.
Monte Ambrose Shenton, 15, Cedar Avenue, Weaste, Manchester.
William Ramsay Sibbald, 5, Manor Road, Hoylake, Birkenhead.
George Smith, M.Sc., 33, Queen Street, Great Harwood, Blackburn.
Thomas William Southron, 32, Casselden Road, Harlesden, N.W. 10.
Joseph Tavroges, B.Sc., 36, Grafton Street, Mile End Road, E. 1.
William Henry Tomlinson, B.Sc., Law Street, Turnpike, Waterfoot, Manchester.
Walter Towse, Woodland Villa, Glastonbury, Somerset.
Henry Marshall Webb, B.Sc., 63, Lancaster Gate, W. 2.
Percy William Weston, 59, Grafton Street, Manchester.
Sidney Edward Whitehead, B.Sc.Eng., 92, Bristol Street, Birmingham.
Charles Williams, B.Sc., 45, Oakington Manor Drive, Wembley, Middlesex.
George Adamson Pemberton Wright, 36, Apsley Road, Clifton, Bristol.

The following Certificates have been authorised by the Council under Bye-Law I (3) for presentation to ballot;

Bhaktabatar Banerjee, M.Sc., 26, Mogul Street, Rangoon, Burma, India.
Amulya Chandra Bose, B.Sc., Sakchi, *viâ* Kalimati, B.N. Rly., India.
Louis Pierre Bosman, University of Capetown, Capetown, S. Africa.
Tarak Prosad Ghose, B.Sc., Dehra Dun, United Provinces, India.

The following papers were read:

"The dilution limits of inflammability of gaseous mixtures. Part III. The lower limits of some mixed inflammable gases with air. Part IV. The upper limits of some gases, singly

and mixed, in air." By H. F. Coward, C. W. Carpenter, and W. Payman.

"The *n*-butylarylamines. Part I. The action of *n*-butyl-chloride on *o*- and *p*-toluidines." By J. Reilly and W. J. Hickinbottom.

"The *n*-butylarylamines. Part II. The nitration products of *n*-butyl-*p*-toluidine." By J. Reilly and W. J. Hickinbottom.

Ordinary Scientific Meeting, Thursday, November 21st, 1918, at 8 p.m., Professor W. J. Pope, C.B.E., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Richard Pendarves Hodges	Dec. 4th, 1913.	Oct. 29th.
Edgar Dingle Jones	May 2nd, 1912.	Nov. 4th.
John Sydney Keel	Feb. 15th, 1917.	Nov. 3rd.

Messrs. S. J. Green and A. L. Bloomfield were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of:

Reginald Christopher Bickmore, 5, Clarence Road, Sydenham Road, Croydon.
Stanley Edward Bowrey, B.Sc., 115, Hainault Road, Leytonstone, E. 11.
Benjamin Richard Heasman, B.Sc., Rutherglen, Throwley Road, Sutton.
Harry Jephcott, M.Sc., 43, King Henry's Road, Hampstead, N.W. 3.
John Parrish, B.Sc. Tech., Ringwood, The Green, Sidcup, Kent.
Ernest Edward Pendlebury, "Moss Bank," 184, Wellington Road, Eccles.
Francis Henry Sweeting Warneford, B.A., B.Sc., 21, Rochester Avenue, Sedgley Park, Prestwich, Manchester.
Leo Daft Williams, 16, Hauteville Court, Stamford Brook, W. 6.
Charles Thomas Woosnam, M.A., 22, Royal Avenue, Lowestoft.

The meeting was then adjourned and the Informal Meeting declared open.

LECTURE.

At the Ordinary Scientific Meeting to be held on Thursday, December 19th, at 8 p.m., the first of the Lectures bearing on the ultimate constitution of matter will be delivered by Professor F. Soddy, M.A., F.R.S., who has chosen as the title of his discourse "The Conception of the Chemical Element as enlarged by the Study of Radioactive Change."

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W., must be received on or before Monday, December 2nd, 1918.

All persons who received grants in December, 1917, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be returned to the Assistant Secretary by Monday, December 2nd.

The Council wish to direct attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Berzelius, J. J. Versuch über die Theorie der chemischen Proportionen und über die chemischen Wirkungen der Electricität; nebst Tabellen über die Atomengewichte der meisten unorganischen Stoffe und deren Zusammensetzungen. Nach den schwedischen und französischen Originalausgaben bearbeitet von K. A. Blöde. Dresden 1820. pp. viii + xvi + 200. From Mr. J. A. Audley.

Bischof, Gustav. Elements of chemical and physical geology. Vol. III. London 1859. pp. xvii + 566.

From Mr. F. J. R. Carulla.

Bone, William Arthur. Coal and its scientific uses. London 1918. pp. xv + 491. ill. 21*s*. net. (*Recd.* 20/8/18.)

From the Publishers: Messrs. Longmans, Green and Co.

Boone, William Thomas. A complete course of volumetric analysis for middle and higher forms of schools. London 1918. pp. viii + 164. ill. 3*s*. 6*d*. net. (*Recd.* 9/7/18.)

From the Author.

Boswell, P. G. H. A memoir on British resources of sands and rocks used in glass-making, with notes on certain crushed rocks and refractory materials. With chemical analyses by H. F. Harwood and A. A. Eldridge. 2nd edition. London 1918. pp. xi + 183. ill. 7*s*. 6*d*. net. (*Recd.* 6/7/18.)

From the Author.

—— A memoir on British resources of refractory sands for furnace and foundry purposes. With chemical analyses by H. F. Harwood and A. A. Eldridge. Part I. London 1918. pp. xii + 246. ill. 8*s*. 6*d*. net. (*Recd.* 22/10/18.)

From the Author.

Chaudhuri, Tarini Charan. Sir William Ramsay as a scientist and man. Calcutta 1918. pp. xii + 66. (*Recd.* 8/7/18.)

From the Author.

Colver, Edward de Wyckersley Swift. High explosives. A practical treatise. London 1918. pp. xxix + 830. ill. £3 3*s*. net. (*Recd.* 17/7/18.)

From the Publishers: Messrs. Crosby Lockwood and Son.

Gatehouse, Frank Brooks. A handbook for cement works chemists. 2nd edition. London 1917. pp. viii + 164. ill. 6*s*. net. (*Recd.* 30/10/18.) From the Author.

Hale, Arthur James. The applications of electrolysis in chemical industry. London 1918. pp. ix + 148. ill. 7*s*. 6*d*. net. (*Recd.* 2/10/18.)

From the Publishers: Messrs. Longmans, Green and Co.

Hofmann, A. W. Introduction to modern chemistry. Experimental and theoretic. Embodying twelve lectures delivered in the Royal College of Chemistry, London. London 1865. pp. xv + 233. ill. From Mr. F. J. R. Carulla.

Institute of Metals. Journal. Vol. I. London 1909. (*Reference.*) [To complete series.] From the Institute.

Kingzett, Charles Thomas. Chemistry for beginners and school use. 3rd edition. London 1918. pp. viii + 211. ill. 2*s*. 6*d*. net. (Recd. 6/7/18.) From the Author.

KNECHT, EDMUND, and HIBBERT, EVA. New reduction methods in volumetric analysis. Reissue, with additions. London 1918. pp. x + 135. ill. 5*s*. net. (*Recd.* 20/9/18.)

From the Authors.

LIEBIG, JUSTUS. Familiar letters on chemistry. Second series. The philosophical principles and general laws of the science. Edited by JOHN GARDNER. London 1844. pp. xii + 218.

From Mr. F. J. R. Carulla.

—— Chemische Briefe. Leipzig 1865. pp. xxviii + 532.

From Mr. F. J. R. Carulla.

MACQUER, PIERRE JOSEPH. Elemens de chimie-theorique. Paris 1753. pp. xxiv + 355 + [xxvi]. ill.

From Mr. F. J. R. Carulla.

MINISTRY OF MUNITIONS. MUNITIONS INVENTIONS DEPARTMENT. Physical and chemical data of nitrogen compounds. Specially compiled for use in connection with the synthesis and oxidation of ammonia. London 1918. pp. 49. (*Recd.* 11/7/18.)

From the Comptroller, M.I.D.

MITSCHERLICH, EILHARD. Practical and experimental chemistry, adapted to arts and manufactures. Translated from the first portion of his compendium by STEPHEN LOVE HAMMICK. London 1838.

From Mr. F. J. R. Carulla.

SMITH, ERNEST A. The zinc industry. London 1918. pp. 231. 10*s*. 6*d*. net. (*Recd.* 17/7/18.)

From the Publishers: Messrs. Longmans, Green and Co.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY MEETING ON THURSDAY, DECEMBER 5TH, 1918.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

ACLAND, LAUCHLAN HENRY PYKE, M.C., Capt. R.E., Island View, Barton-on-Sea, Hants. Assistant to Dr. Rideal, Mr. E. R. Bolton, and Mr. W. N. Simmons in turn. Now employed in connexion with gas warfare. Sometime Exhibitioner of Magdalen College, Oxford. B.A. with honours in chemistry. Paper with Dr. Rideal on "Oils of Ceara and *Funtumia elastica*," in *Analyst*, 1913. Unpublished technical research with Mr. Bolton. Work on gas warfare. (*Signed by*) Arthur W. Crossley, Paul Murphy, H. B. Baker, E. Richards Bolton, *George Beilby*.

ANDERSON, VALENTINE GEORGE, 31 Victoria Avenue, Canterbury, Victoria, Australia. Consulting chemist. Certificated assayer, School of Mines, Ballarat, Australia. Victorian Government Research Scholar in Chemistry,

University of Melbourne (1912–1915). Formerly demonstrator in chemistry, School of Mines, Ballarat, and lecturer in chemistry, Melbourne Technical School (Working Men's College). Author of paper on "The Influence of Weather Conditions upon the Amounts of Nitrogen Acids in the Rainfall, at and near Melbourne, Australia," "Q. Journal of the Royal Meteorological Society," vol. xli., April, 1915, pp. 99–116. See also "Annual Reports of Progress of Chemistry," 1915, pp. 210–211. For further work on same subject see Reports British Association, 1915, p. 87–94; 1916, pp. 128–130. (*Signed by*) D. Avery, Orme Masson, Heber Green, Gilbert Rigg, W. Russell Grimwade.

BAILLIE, WILLIAM LEARMOUTH, 70, Hampton Road, Clifton, Bristol. Technical and analytical chemist, on the staff of the Director of Chemical Inspection, Royal Arsenal, Woolwich, S.E. 18. Hope Prize Scholar, Vans Dunlop Scholar, and assistant in chemistry in Edinburgh University. Now senior chemist on above staff, and engaged for over two years on confidential analytical and research work. (*Signed by*) James Walker, Sydney A. Kay, Alex. C. Cumming, Leonard Dobbin, H. Gordon Rule, J. P. Longstaff, Oliver Trigger, A. Vincent Elsden.

BAINBRIDGE, FRANK, Woodland View, West Road, Loftus-in-Cleveland. Chief chemist (metallurgical and fuel), Messrs. Skinningrove Iron Co., Saltburn-by-Sea. Pupil under Messrs. Pattinson and Stead, Middlesbrough, 1906–1911. Metallurgical chemist, Messrs. Skinningrove Iron and Steel Co., Saltburn, 1911–1915. Chief chemist at Skinningrove Iron and Steel Co., 1915 to present day. At present engaged on a research, "Fluorspar and Basic Slags" (Carnegie Research Scholarship). (*Signed by*) Alfred Hutchinson, Ernest Bury, J. E. Stead, H. Frankland, C. H. Ridsdale, *Ernest W. Jackson, N. D. Ridsdale.*

BALLS, ERNEST GEORGE, M.C., R.E., B.Sc., Orford House, Wellington Road, Wanstead, E. 11. At present Lt. R.E. In normal times teacher. London Univ. B.Sc., 1st Class pass. London Univ. B.Sc., Honours Chemistry. Research in organic chemistry in conjunction with C. Hollins, Esq., B.Sc., for three years; it was brought to an end by the war. (*Signed by*) J. Wilson, C. Hollins, J. L. White, *W. H. Simmons, J. Hart-Smith.*

BARRS, PERCY, 33, Lancaster Park, Richmond Hill, Richmond, Surrey. Manufacturing chemist, charged with the analytical control of Messrs. Lot, Ltd., manufacturing chemists, W. 8. Advisory chemist to Messrs. Gaston, Williams and Wigmore, London, E.C. (contractors to H.M. Government). Educated at Hulme Grammar School, Manchester (winner of the Hulme Science Scholarship, 1897). In practice as a clinical analyst for eleven years past. Sometime pupil of F. Filmer De Morgan, F.C.S. Edinburgh Heriot-Watt medallist. Studied chemistry at the Metropolitan College of Chemistry under W. Watson Will, F.C.S., Ph.C., in 1904, and continued these studies under H. Lucas, F.C.S., Ph.C., at the South of England College of Pharmacy. Passed the final examination of the Pharmaceutical Society of Great Britain, 1912, the subjects including chemistry and physics. Member of the Pharmaceutical Society of Great Britain. Member of the British Pharmaceutical Conference. Keenly desirous of keeping in touch with analytical and process chemistry, to attend the meetings of the Chemical Society, to receive its publications regularly, and to come in contact with its fellows. (*Signed by*) F. W. Crossley-Holland, Archibald Macpherson, J. Wicliffe Peck, F. Filmer De Morgan, W. H. Martindale.

BLAINE, WILLIAM ANDREW STEWART, Ardbana Crescent, Coleraine. Science master. Chemical education at King's College, London, and Royal College of

Science, Dublin. B.Sc.(London), 1911. Associate of King's College, 1912. Science master at the Rainey Endowed School, Magherafelt, for four years, 1912–16. Senior science master at the Academical Institution, Coleraine, for last two years. Lecturer in industrial chemistry under Antrim County technical scheme, 1914–1918. (*Signed by*) Herbert Jackson, G. T. Morgan, Patrick H. Kirkaldy, L. E. Hinkel, A. W. H. Upton.

BRIGHT, JOHN HAROLD, 157, Greenvale Road, Eltham, S.E. 9. Analytical chemist. Five years' experience with Mr. Alex. E. Tucker, F.I.C., F.C.S., of 55, Station Street, Birmingham (one year as chief assistant), now engaged as junior assistant chemist, Directorate of Chemical Inspection, Woolwich. (*Signed by*) R. B. Pettigrew, Robt. L. Brown, Frank N. Harrap, *S. C. Atkinson*, *Alex. J. Boyd.*

BRITTON, HUBERT THOMAS STANLEY, Lynn Dene, Court Road, Kingswood, Bristol; present address: 71, Allen Road, Wolverhampton. Chemist (examiner in Aeronautical Inspection Department). Bachelor of Science, University of Bristol, 1914. Subjects: Chemistry, Physics, Mathematics. Since July, 1916, I have been engaged in the examination of aeroplane dopes and their ingredients. (*Signed by*) F. Francis, J. W. McBain, F. W. Rixon, J. Wertheimer, T. H. Mallagh.

BRITTON, REGINALD PERCY LEOPOLD, 58, The Crescent, Wimbledon Park, S.W. 19. Technical chemist. Nine years as chemist in paint and varnish industry. Desire to use the library of Chemical Society. (*Signed by*) Henry M. Hatherly, Hubert R. Wood, Simon Solomon, H. Houlston Morgan, *W. S. Simpson.*

BUCKLEY, CHARLES DANIEL, 52, Gilda Brook Road, Eccles. Consulting chemist (since being with the Bayer Co.), at 18, Booth Street, Manchester. Passed honours grade in chemistry, Rochdale Technical, also honours grade, bleaching, dyeing, Salford. Chemist at Dan. Lee and Co., Castleton, then extensive research work in vat colours, processes in use. Chemist to Bayer Co. for sixteen years, part of this time research work at Leverkusen, Germany. (*Signed by*) Lionel G. Larmuth, R. Ernest Jackson, Percy Bean, E. J. Wilkinson, William Marshall.

COFMAN-NICORESTI, JULES, 15, Speenham Road, S.W. 9. Assistant analyst. Member of the Pharmaceutical Society of Great Britain. Studied bacteriology under S. G. Paine, D.Sc., F.I.C., at the South-Western Polytechnic Institute. Employed by the Society of Apothecaries of London in their analytical and bacteriological laboratory. (*Signed by*) E. A. Atkins, G. H. Martin, Charles Wesley Bayley, H. Lucas, Gerald Druce.

COPISAROW, MAURICE, M.Sc., University, Manchester. Research chemist in Department of Industrial and Scientific Research, and analytical chemist in Department of Explosives Supplies. Author of following papers:— "Note on Triphenylcarbinol and its Formation," *Proc. Chem. Soc.*, 1914. "Carbon: its Molecular Structure and Mode of Oxidation," *Memoirs Manch. Lit. and Phil. Soc.*, 1915. "Trinitrotoluene," *Chem. News*, 1915 and 1916. "The Friedel-Crafts Reaction," Part I. *J.C.S.*, 1917. "Phthalides of the Benzene, Naphthalene, and Carbazole Series," Part I., in conjunction with C. Weizmann, *J.C.S.*, 1915 (*Signed by*) Harold B. Dixon, Arthur Lapworth, F. P. Burt, J. E. Myers, Henry Stephen, W. K. Slater.

CROFT, CYRIL MURTON, 37, Rusholme Road, Putney, S.W. 15. Civil engineer. Assistant engineer at the Wandsworth, Wimbledon, and Epsom District Gas Co., and works manager of the Wandsworth Gas Works. My professional duties bring me into close touch with the latest developments of chemical science, and I am anxious to maintain this connexion with the

assistance to be obtained from the Society's Journal and the meetings at Burlington House. (*Signed by*) Charles S. Garland, J. A. Pickard, Henry Atlas, *H. Shulman*, *P. J. Fryer*.

DAVIES, JOHN EDWYN, Taimawr, Swansea Road, Merthyr Tydvil. Chemistry master at a technical school. B.Sc. (London). Associate of Reading University College, and pass in higher chemistry. Honours certificate in inorganic and organic chemistry (Board of Education). Thirteen years' experience teaching advanced chemistry. (*Signed by*) J. W. Shepherd, Robt. D. Abell, John Hanley, *R. W. Atkinson*, *W. Briggs*.

DIAMOND, CLAUDE, 17, Moresby Road, Upper Clapton, London. Analytical chemist. Bachelor of Science of the University of London, first division, with chemistry one of the subjects. For last four years on chemical staff of Pritchett and Gold Electrical Power Storage Co., Ltd., Dagenham Dock, Essex, accumulator manufacturers. At present time preparing for honours chemistry at Birkbeck College. (*Signed by*) George Senter, Fred Barrow, Gerald H. Martin, H. D. K. Drew, *G. D. Lander*.

DONALDSON, HERBERT HECTOR, 15, Ash Leigh, Anfield, Liverpool. Analytical chemist, Liverpool City Engineers' Laboratory. Board of Education certificates, inorganic and organic chemistry. Experience in gas works analysis, and also in chemical analysis in sugar refinery. Now engaged in analysis of poultry foods, and manures made from waste vegetable products. (*Signed by*) E. C. C. Baly, R. Robinson, H. H. Froysell, J. Lea, G. S. Irving.

DOODSON, JOHN EDWARD, Smithy Bridge, Nr. Rochdale, Lancs. Works chemist and managing director of bleaching, dyeing, and sizing works. Two and a-half years day course at the Manchester College of Technology; 1st Class Hons. in Chemistry, 1895; three years works chemist in coal tar colour works; eighteen years works chemist in bleaching, dyeing, and sizing works. (*Signed by*) William Marshall, Robert A. Oddy, W. J. Lund, Samuel M. Walford, Robert W. Oddy.

DOUGLAS, JOHN ROBERT, West-field, Saltcoats, Ayrshire, N.B. Technical chemist. Associate of Royal College of Science for Ireland, 1910; Associate of Institute of Chemistry, 1912; in the employment of Messrs. Nobel's Explosives Co., Ardeer Factory, Scotland, as technical chemist, 1912 to present time. (*Signed by*) Wm. Rintoul, N. Picton, E. Wheeler, T. W. Price, R. A. Joyner.

DU PAIN, GEORGE ZEPHIRIN, "Symington," Parramatta Road, Ashfield, Sydney. Teacher of physical education. Trained in chemistry by competent private tutors in the usual theoretical and practical work covered by college or university syllabus; studied advanced theoretical and practical organic chemistry at Sydney Technical College; for past nine years continuously carrying out physiological and food analyses and experimental work in my own laboratory, the equipment of which cost about £500. Keenly desirous of keeping in touch with latest researches in chemical science. Member of Australian Chemical Institute. (*Signed by*) Richard W. Challinor, Henry G. Smith, Archibald D. Ollé, G. Spurge, H. G. A. Harding.

EVANS, HERBERT JOHN, 7, Market Street, Haverfordwest. Public analyst and consulting chemist. B.Sc. (Wales), F.I.C.; public analyst for the counties of Brecon and Radnor; Lieut., R.F.A. (*Signed by*) Alex. Findlay, T. Campbell James, Alfred Holt, *Alfred Smetham*, *Francis J. Dymond*, *F. C. Guthrie*.

FALCONER, CAMPBELL, The Hall, Osbaldwick, Nr. York. Manufacturing and analytical chemist; also pharmacist. Manager and chemist to Messrs. Falconer and Co., manufacturers of caramel, farina, essential oils, etc.;

analyst and adviser to Messrs. Lancelot, Foster and Sons, feeding stuffs and manure manufacturers and agricultural merchants, York; formerly clinical chemist at the Jessop Hospital for Women, Sheffield; special research, "Estimation of the Nitrogen Ammonia Coefficients in the Metabolic Diseases of Pregnancy, and abstraction of Organic Acidity of the Urines of Cases of Glycosuria." (*Signed by*) A. R. Gower, John Taylor, Arthur Adams, *Richard Spencer, C. W. Priestley, Charles Huxtable.*

Foster, James, 59, Elizabeth Street, N. Woolwich, E.16. Student at Battersea Polytechnic, Chemical Department (evening classes, 1901–1910), and at East Ham Technical College; twenty years technical experience in the oils, fats, distillation of tar, and allied industries. (*Signed by*) John Wilson, J. L. White, A. E. Dunstan, F. B. Thole, *J. H. Johnston, J. Hart-Smith.*

Gates, Alfred Edwin, 32, Conway Road, Luton, Beds. Technical manager and chemist (dyeing, bleaching, and chemical manufacture). Member of the Pharmaceutical Society, and for the past six years works chemist and manager in a large dyeing and bleaching works, also manufacturing several important chemical products for technical and medicinal purposes. (*Signed by*) Reginald B. Brown, Alfred C. Young, Bertram Blount, *Geoffry Martin, Walter F. Reid.*

Gepp, Herbert William, Hobart, Tasmania. General manager. Ten years, 1896–1906, in explosives manufacturing industry, Victoria and Scotland, mainly with Nobel's Explosives Co.; seven years at Broken Hill, N.S.W., in acid manufacturing and in development flotation work, mainly as general manager, Amalgamated Zinc (de Bavay's, Ltd.), Broken Hill, N.S.W.; since 1914 engaged in munition and metal work in U.S.A. and Australia; now general manager, Electrolytic Zinc Co. of Australasia. (*Signed by*) D. Avery, Heber Green, Orme Masson, W. Russell Grimwade, C. S. Dawes.

Gladding, Geoffrey, M.Sc., 4, Heaton Road, Heaton Norris, Stockport. Research chemist in Messrs. Hardman and Holden, Miles Platting. B.Sc., 1st Class Honours, University of Manchester; M.Sc. by thesis, "Chlor-methyl Alcohol and some of its Condensation Products." (*Signed by*) Harold B. Dixon, Arthur Lapworth, Henry Stephen, W. K. Slater, F. P. Burt, Norman Smith.

Grant, George, "Tinniver," Balmoral Avenue, Cathcart, Glasgow. Technical chemist and assistant general manager. Student for two years under R. R. Tatlock and Thomson, Glasgow; assistant to above firm for four years; assistant in charge of students' department for one year (1913–1914); chief assistant in laboratories of R. R. Tatlock and Thomson; for one and a-half years (1916–1918) chemist to Blacklock and Macarthur, Ltd., colour manufacturers, Glasgow, from March to September, 1918; now technical chemist and assistant general manager, Messrs. Victors, Ltd., chemical manufacturers, Stalybridge; brought out a raw linseed oil substitute during my researches while chemist to Blacklock and Macarthur, Ltd., Glasgow. (*Signed by*) R. R. Tatlock, G. G. Henderson, Thomas Gray, R. T. Thomson, James Booth, John Turnbull, James McAlley.

Green, John Russell, 2, Belmont Park, Lee, S.E.13. B.Sc.(Lond.); works chemist; at present Captain, 10th (S) Bn. the Hampshire Regt. From April, 1913, to October, 1914, when I joined the Army, I was chief works chemist to Messrs. Batchelor and Co., Ltd., Llanelly, S. Wales; prior to April, 1913, I was demonstrator to the late Sir W. Ramsay's practical chemistry class, and was conducting an investigation into complex mercury compounds; this was left unfinished owing to my leaving University College, London; I

wish to further my knowledge of chemistry. (*Signed by*) Frank Collingridge, W. B. Tuck, J. N. Collie, F. G. Donnan, S. Smiles.

HAIGH, WILLIAM DUTHIE, 15, Cavendish Avenue, Church End, Finchley, N.3. Research chemist under the Department of Scientific and Industrial Research. B.A., B.Sc.(N.U.I.) Chemistry; Associate of the R.C.Sc., Ireland (applied chemistry) and A.I.C.; chemist to the Geological Survey, Ireland, 1909–12; on staff of the Royal College of Science, Ireland, 1912–1918; "A Method for the Estimation of Hygroscopic Moisture in Soils," Proc., R.D. Soc., 1915; "The Volcanic Rocks of Phillipstown," Proc., R.I.A., 1914; "Interbasaltic Rocks and Iron Ores of N.E. Ireland," memoir, Geol. Survey, Ireland, 1912. (*Signed by*) G. T. Morgan, Herbert Jackson, Herbert Savage, H. F. Coward, H. M. Atkinson, A. J. Hale.

HEPWORTH, HARRY, Nobel's Explosives Co., Stevenston, Scotland. Works chemist. B.Sc.(Lond.), 1st Class Hons. Chemistry, 1914; M.Sc.(Lond.), "On the Stereochemistry of the Oximes"; A.I.C. Branch of Organic Chemistry; F.I.C., 1918; research work with Prof. F. S. Kipping, Univ. Coll., Nottingham, 1914 and 1915; Propulsive Dept., Nobel's Explosives Co., 1915 to present time. (*Signed by*) William Rintoul, William Barbour, G. H. Beckett, Thomas J. Nolan, Norman Picton, T. W. Price.

HOWARD, HERBERT LESLIE, 44, Disraeli Rd., Forest Gate, E.7. Analytical and works chemist. I am a registered student of the Institute of Chemistry, Inter.B.Sc.(Lond.), and now proceeding to Honours B.Sc. (Chem.); in all, seven years' study (practical and theory) of chemistry, and nearly five years' experience as works chemist to three different firms. (*Signed by*) Frank E. Weston, George Senter, A. Molteni, *Frank G. Pope*, *E. Richards Bolton*.

JAGO, WILLIAM CLAUDE, 17, Wilbury Avenue, Hove, Sussex. Lieut., R.F.A.(T.); analytical and consulting chemist and bacteriologist. Studied and acted as assistant for some years with William Jago, sen., F.I.C., F.C.S., and also with Professor Jörgensen, of Copenhagen; subsequently practised on own account until obtaining a commission in his Majesty's Forces on November 15th, 1916; since then has acted as gas defensive instructor until sent, on active service, overseas in December, 1917, and then took on the duties of divisional artillery gas officer until entering hospital; joint-author of "The Technology of Bread-making." (*Signed by*) William Jago, M. C. Clutterbuck, W. H. Gibson, Julian L. Baker, Henry F. Everard Hulton.

JEFFS, BERNARD ARTHUR JAMES, 35B, Gladstone Avenue, Wood Green, N.22. Student of chemistry at the Technical College, Finsbury, London, E.C.2. As a second-year student of chemistry at the City and Guilds of London Institute, I am very desirous of keeping in touch with current literature. (*Signed by*) G. T. Morgan, Arthur J. Hale, H. M. Atkinson, Percy Edgerton, Walter A. Voss.

JOHNS, COSMO, Burngrove, Pitsmoor Road, Sheffield. Metallurgical engineer. Melting house manager, Vickers, Ltd., Sheffield; director, Oughtibridge Silica Fire Brick Co., Ltd., nr. Sheffield; superintending manufacture of special steel for armament work; member of Council of Faraday Society; communications to *Journ. Iron and Steel Institute*, *Journ. Institute of Metals*, *Journ of Soc. Chemical Industry*, *Geological Magazine*, *Proceedings of the Faraday Society*, *Transactions Ceramic Society*. (*Signed by*) Cecil H. Desch, H. B. Weeks, Thomas Turner, Richard Seligman, E. L. Rhead.

JUDD, CLIFFORD WILLIAM, Maythorne, Ardrossan Road, Saltcoats, Ayrshire. Technical chemist. B.Sc.(Wales); part-author of "The Addition of Negative Radicles to Schiff's Bases" (*Trans.*, J.C.S., 1914, **105**); technical

chemist at Nobel's Explosives Co., Stevenston, Ayrshire. (*Signed by*) Alex. Findlay, T. Campbell James, Wm. Rintoul, T. W. Price, G. H. Beckett, Wm. Barbour, Thos. J. Nolan.

KEEBLE, EDWIN PERCY, Summer Lodge, Kenilworth. Departmental manager of British Portland Cement Manufacturers, Ltd. Chiefly scholastic, having specialised in chemistry at Oundle School and in practical way at Cambridge, and since then as amateur and student, keeping up to date with current literature. (*Signed by*) A. C. Davis, S. G. S. Panisset, H. K. G. Bamber, *R. H. Harry Stanger*, *S. Dickson*.

KETTEL, FREDERICK JOHN, 47, Limes Road, Beckenham, Kent. Lecture assistant in the Chemical Dept., University College, since 1909. (*Signed by*) F. G. Donnan, J. N. Collie, Henry A. Miers, Samuel Smiles, H. Gordon Bibby.

KILBY, THOMAS, 1, Westfield Road, Toller Lane. Bradford. Works chemist and manager. Six years' studentship, Bradford Technical College, Chemistry Dept.; seven years West Riding County Analyst's Laboratory; fifteen years chief chemist, D. Salmond and Neph., Bradford (soap, oil, and glycerine manufacturers); two years manager, D. Salmond and Neph., Bradford. (*Signed by*) F. W. Richardson, Walter M. Gardner, Barker North, G. W. Slatter, *B. A. Burrell*, *J. R. Denison*.

KNIBBS, NORMAN VICTOR SYDNEY, Melbourne, Australia. Chief chemist, H.M. Factory, Langwith. B.Sc., Melbourne; A.I.C.; Kernot Final Honours Scholarship in Chemistry; chemist in D.E.S. M. of M., since October, 1915; now chief chemist at above factory. (*Signed by*) John Mitchley, E. Taberner, A. C. D. Rivett, C. W. Bailey, *A. Geake*.

LE BROCQ, LAURENCE FRANCIS, "Akender," Guildford Road, South Farnboro', Hants. Assistant chemist, Royal Aircraft Establishment. Bachelor of Science (London), 1st Class Pass; Associate of Institute of Chemistry; one year's experience (works) of analytical and research chemistry (inorganic) at private firm; two years' experience of analytical and research chemistry (mainly organic) at Royal Aircraft Establishment. (*Signed by*) J. B. Coleman, J. C. Crocker, F. H. Lowe, Gilbert Palmer, A. U. Newton, H. Arwel Thomas.

LITTLEWOOD, ERNEST ALFRED, 12 Brookfield Road, Crumpsall, Manchester. Works chemist. Associate Manchester School of Technology; diploma in general chemistry and chemical technology; matriculated, London University, 1908; chief assistant, sulphur colours department, with Messrs. Levinstein, Ltd., Manchester, 1903–1918; members of Soc. Chem. Ind. and Soc. of Dyers and Colourists. (*Signed by*) Herbert Levinstein, Trevor O. Morgan, Thomas Callan, Jas. A. Russell Henderson, Robert Barton.

LOO, SHIH CHEN, 70, High Lane, Chorlton-cum-Hardy, Manchester. Associate of the College of Technology, Manchester; research student in chemistry. Student of chemistry for three years in the College of Technology; one year research student in the Owens College. (*Signed by*) H. B. Dixon, W. K. Slater, Henry Stephen, S. J. Peachey, E. L. Rhead.

MCARTHUR, DONALD NEIL, 28, Grafton Street, Glasgow. Lecturer in chemistry. Graduated as Bachelor of Science (B.Sc.), Glasgow University, 1913; Associate of Institute of Chemistry (A.I.C.); lecturer in chemistry, West of Scotland Agricultural College; and chemist to "Glasgow and West of Scotland Radium Committee." Publications: Patterson and McArthur, *J.C.S.*, 1915, T., 814–815; Berry and McArthur, *J.S.C.I.*, 1918, T., 1–5. (*Signed by*) Cecil H. Desch, T. S. Patterson, A. W. Stewart, G. G. Henderson, Reginald A. Berry, Alexander Fleck.

McKerrow, John Armour, 2, Kymer Villas, Kidwelly, Carmarthenshire. Works chemist, Cordite Section of H.M. Factory, Pembrey. M.A., B.Sc., A.I.C.; the B.Sc., professing chemistry as principal subject; the A.I.C. granted for war work; formerly science demonstrator in Stowe College, Glasgow, and teacher of Science in Airdrie (1908–10), Irvine, and Paisley secondary schools (1912–15). (*Signed by*) Ernest Vanstone, Walter R. Moore, R. J. Hughes, A. J. Leigh, E. J. Amies.

Maries, Charles Stewart, Eggesford Cottage, Queen's Road, Aldershot. Assistant works chemist. Four years' training at University College, Reading; degree of B.Sc.(Lond.) obtained; three years as assistant works chemist at the tar works, S. Metropolitan Gas Co. (*Signed by*) Henry Bassett, jun., Henry Bassett, Gerald Druce, *H. A. D. Neville, Samuel Smiles.*

Matthews, Norman Louis, 45, Tyrwhitt Road, Brockley, London, S.E.4. Student of applied chemistry at City and Guilds Technical College, Finsbury. Being a second year chemical student at the above College, I am desirous of keeping myself acquainted with the modern advances of chemistry and of being able to attend the Society's meetings, besides having access to the library. (*Signed by*) G. T. Morgan, William R. Grist, H. Singer, A. J. Hale, W. H. Prince, Charles M. Stuart.

Moore, Robert Alfred, 6, Sunbury Avenue, West Jesmond, Newcastle-on-Tyne. Analytical chemist employed by Royal Society War Committee. Oxford Senior Local, 1st Class Hons., 1913; London Inter. B.Sc., July, 1914; Armstrong College (University of Durham), B.Sc., June, 1918 (with 2nd Class Hons. in Chemistry); analytical chemist engaged in tar testing, August, 1916—. (*Signed by*) P. Phillips Bedson, F. C. Garrett, J. A. Smythe, *Frederick N. Binks, S. Hoare Collins.*

Mountford, Albert Victor, 38, Gamblins Road, St. Martins, Christchurch, N.Z. Tannery chemist. Formerly student of inorganic and organic chemistry at Canterbury College, Christchurch; for four years chemist to the Woolston Tanneries, Ltd., New Zealand, employing over 200 hands. (*Signed by*) Thomas H. Easterfield, Robert English, George Gray, *B. C. Aston, J. S. Maclaurin.*

Newton, William, Station Road, Wootton Bassett, Wilts. Manager of creamery and condensing factories. Five years studying chemistry and other subjects at Harris Institute, Preston, College of Technology, Manchester, and Kingston College, qualifying for National Diploma of Agriculture and National Diploma of Dairying; later analyst to Trufood, Ltd.; my occupation is intimately connected with analytical chemistry. (*Signed by*) Jas. Grant, R. L. Taylor, S. J. Peachey, *F. S. Sinnatt, E. L. Rhead.*

Norbury, Douglas, Lyndene, Lansdowne Road, West Didsbury, Manchester. Chemist to the Greenfield Bleaching Co. Studied two sessions (1912–1914) at Royal Technical Institute, Salford; two years practical textile analysis. (*Signed by*) Ernest Clark, J. R. Appleyard, B. Prentice, Norman Cooke, William McCleary.

Nurse, Edwin Hart, "Southwold," Lewis Road, Sutton, Surrey. Analytical chemist (at present serving as Lieutenant, R.A.F.). Studied chemistry at S.W. Polytechnic, Chelsea, three years (1912–1915); took London University B.Sc. (1st Class Honours in Chemistry) in 1915; at Government Lab., London, 1915–1917 (steel analysis); at present working as Lieutenant, R.A.F., in R.N. Airship Service; hydrogen officer on iron contact hydrogen plant since June, 1917. (*Signed by*) J. B. Coleman, J. C. Crocker, F. H. Lowe, J. J. Fox, P. J. Sageman.

Obroi, Mehtab Singh, Rawal Pindi (India). Demonstrator in physics and

chemistry and botany and zoology, Gordon College, Rawal Pindi. B.Sc. of the Punjab University; author of "Tables on Chemical Analysis." Past experience as a teacher of physical science, at Murree Riwaz High School, for one year; manufacturer of inks, boot-creams, and other important chemicals; two years' experience as demonstrator in chemistry, Gordon College, R. Pindi. (*Signed by*) Horace B. Dunnicliff, Hashmar Rai, Puran Singh, Sher Singh, *Ruchi Ram Sahni.*

PARKER, LESLIE HENRY, "The Chestnuts," Church Road, Leatherhead, Surrey. Research chemist; Lieut., Royal Engineers. M.A.(Cantab.), D.Sc.(Lond.), A.I.C.; member of the Society of Chemical Industry; elected to "Beit Fellowship for Scientific Research," Sept., 1914; research at Imperial College of Science and Technology, 1912–14; author and joint-author of papers in *Trans.*, 1913, 1914, 1918; research for Ministry of Munitions on the nitrogen problem, and joint-author of unpublished reports on same. (*Signed by*) H. B. Baker, J. R. Partington, Eric K. Rideal, H. C. Greenwood, J. A. Harker.

PATERSON, JOHN, 1, Rowallan Gardens, Glasgow, W. Founder and managing director of John Paterson and Co., Ltd., manufacturing chemists, Henrietta Street, Glasgow, E. Chemical manufacturer and manufacturing chemist. (*Signed by*) James McCutcheon, James Macleod, Robert Mathieson, *John Glaister, Gilbert J. Alderton, W. H. Simmons.*

PHEASEY, WILFRED STANLEY, B.E.F. (no home address). Chemical adviser, IInd Corps. Inter B.Sc.(Lond.), B. and E. certifs. in chemistry, adv. inorg. and org. (theor. and pract.); physics (adv. heat, sound, light, mag., and elec.); mathematics, Stage VII., drawing, etc.; three years' works experience, including research on celluloid substitutes, tin residues, etc., for private firm. (*Signed by*) Hamilton McCombie, G. W. Monier-Williams, J. P. Longstaff, *E. H. Tripp, Arthur R. Ling, E. F. Armstrong.*

PORTER, ALEXANDER PARK, 157, Greenvale Road, Eltham, S.E.9. Analytical chemist, junior assistant chemist (tempy.), The Directorate of Chemical Inspection, Royal Arsenal, Woolwich. Junior assistant, Messrs. Wm. Beardmore and Co., Parkhead Forge, Glasgow; assistant in Chemical Dept., The West of Scotland Agricultural College, Blythswood Square, Glasgow; assistant chemist to Messrs. the Burmah Oil Co., Ltd., in their refinery in Rangoon, Burma; engaged in rubber analysis; rank, junior assistant chemist (temp.), The Directorate of Chemical Inspection, Royal Arsenal, Woolwich. (*Signed by*) R. B. Pettigrew, Frank N. Harrap, Robert L. Brown, *S. C. Atkinson, Alex. J. Boyd.*

PRATT, JOSEPH FRANCIS, 77 Hanbury Road, Pontnewynydd, Mon. Chief analytical chemist and test-house manager, c/o The Pontnewynydd Sheet and Galvanising Co., Ltd. Three and a-half years assistant to Walter Macfarlane, F.I.C., Wednesbury; three years works chemist under P. W. Hill, F.C.S., Patent Shaft and Axletree Co., Ltd., Wednesbury; three years works chemist, H. R. Marsden, Ltd., Leeds; six months present employers in capacity stated above. Exam. successes: Board of Education Inor. Chem. (Theo. and Pract.), Stage II., 1911; metallurgy (theo. and pract.), Stage III., 1911: Iron and Steel Manufacture, City and Guilds of London Institute of Technology, Hons. Grade, 1912; 1st Hons. Silver Medal and 2nd Bronze Medals for proficiency in iron and steel manufacture; full technological certificate; have attended instruction in Stage III. chemistry at West Bromwich and Leeds; am desirous of keeping in touch with latest advances of chemical science. (*Signed by*) Percy W. Hill, R. Lloyd Whiteley, Frank E. Thompson, *J. H. Duncan, F. Gwilym Trehane.*

Pugh, Ralph John, 99, Lonsdale Road, Barnes, S.W.13. Managing director, London Chemical Works, Ltd. Period 1911–1914: invention of successful chemical process for the manufacture of spirmabel and paper-making fibre from the common stinging nettle (*Urtica dioica*), comprising three years' research work. Period 1915 to date: responsible for design and installation of successful plant for the manufacture of B.P. salicylic acid and B.P. sodium salicylates and other derivatives on a large scale. (*Signed by*) Charles Alex. Hill, C. F. Cross, Francis H. Carr, *W. A. H. Taylor, Edward Bevan.*

Purves, George Thomson, A.M.Inst.C.E., "Thirlestone," Chryston, nr. Glasgow. Manager of by-product coking plant. Chief assistant, public analytical laboratory (two years); works chemist (three years); assistant manager and chemist, gas works (seven years); manager, by-product coking plant (six years). Papers: "Application of Coke Oven Practice to Gas Works," "Fractional Collection of Crude Tar," "Extraction of Tar Fog from Hot Gas," "On Benzol and Ammonia Production in Coal Carbonisation." (*Signed by*) G. G. Henderson, Cecil H. Desch, Thomas Gray, James Macleod, R. T. Thomson.

Ridge, Dudley, 7, College Place, Brighton, Sussex. Student of analytical chemistry. Intermediate B.Sc. (Lond.); preparing for B.Sc. Final (probably honours in chemistry). (*Signed by*) K. G. Laiwala, M. C. Clutterbuck, W. H. Gibson, *William Jago, W. H. Simmons.*

Robertshaw, George Frederick, "Mornay," Kearsley Road, Hr. Crumpsall, Manchester. Works chemist (head of leather specialities department). Chief chemist to oil department, Levinstein, Ltd.; Associate of the Municipal College of Technology (Chemistry and Chemical Technology Diploma); City and Guilds silver and bronze medallist, bleaching and dyeing, respectively; member of Soc. of Chemical Industry. (*Signed by*) Herbert Levinstein, Arthur G. Green, Trevor O. Morgan, Robert Barton, Frederic Robinson, Jas. A. Russell Henderson, Thomas Callan.

Rowe, Frederick Maurice, 5, Woodbine Terrace, Latchford, nr. Warrington. Research chemist and lecturer. B.Sc. (Leeds), 1st Class Hons. in colour chemistry; diploma in dyeing (Leeds); Leblanc medallist, 1911; M.Sc. (Leeds), 1912; research fellow (Leeds), 1912–13; research chemist, Messrs. Jos. Crosfield and Sons, Ltd., 1913–16; for the past two years research assistant to Prof. A. G. Green in the Dyestuffs Research Laboratory, College of Technology, Manchester, and lecturer in dyestuffs in the University of Manchester. Publications: "The Alkaline Condensations of Nitrohydrazo-compounds. Part II.," *Trans.*, **101**, 2003; Part III., *Trans.*, **101**, 2443; "Quinonoid Salts of *o*-Nitroamines and their Conversion into Oxadiazole Oxides," *Trans.*, **101**, 2452; "Quinonoid Salts of Nitroanilines," *Trans.*, **102**, 508; "Constitution of Oxadiazole Oxides," *Trans.*, **102**, 897; "Conversion of *o*-Nitroamines into *iso*Oxadiazole Oxides," *Trans.*, **102**, 2023; "Conversion of *o*-Nitroamines into *iso*Oxadiazole Oxides and of *o*-Nitrosoamines into *iso*Oxadiazoles," *Trans.*, **111**, 612; Nitro-derivatives of *iso*Oxadiazole Oxides and of *iso*Oxadiazoles," *Trans.*, **113**, 67; "The Chemistry of the Sulphide Dyestuffs," *J. Soc. Dyers and Col.*, **33**, 9. (*Signed by*) Arthur G. Green, A. G. Perkin, J. B. Cohen, H. M. Dawson, S. J. Peachey.

Salmon, Walter, 17, The Grove, Eccles, nr. Manchester. Analytical chemist. In charge of organic laboratory for the past seven years, both analytical and manufacturing (food products). (*Signed by*) Robert Pettigrew, James Porter Shenton, Henry Garnett, *William Thomson, A. W. Cowburn.*

Shenton, Monte Ambrose, 15, Cedar Avenue, Weaste, Manchester.

Chemist at the Henry Wells Oil Co., Bloom Street, Salford, Manchester. Student of pure and applied chemistry at the Royal Technical Institute, Salford, 1909–1914; assistant chemist to the Henry Wells Oil Company for two years; chief chemist to the Henry Wells Oil Company at present and for the last two and a-half years. (*Signed by*) Ernest Clark, J. R. Appleyard, B. Prentice, A. Potter, *Vernon Edge*.

SIBBALD, WILLIAM RAMSAY, 5, Manor Road, Hoylake, Cheshire. Works research and experimental chemist (vegetable oils, oil-seeds, and by-products). Three years student and assistant with Messrs. R. R. Tatlock and Thompson (Glasgow); fifteen years works chemist, etc., with Messrs. R. Silcock and Sons, Liverpool; London Intermediate B.Sc. examination (chemistry, botany, geology, mathematics); lecturer in building science (January, 1918) (chemistry and physics), Liverpool Central Technical School. (*Signed by*) Cecil Revis, George Tate, Thomas J. Roberts, *Arthur A. Dallman*, *Alfred Smetham*.

SINKINSON, ERIC, 14A, Albert Bridge Road, S.W.11. Demonstrator in chemical technology at the Imperial College of Science and Technology, South Kensington. Four years student in Chemical Dept., University of Sheffield; one year private assistant to Prof. L. T. O'Shea (Sheffield University); one year demonstrator in non-ferrous metallurgy under Prof. J. O. Arnold, F.R.S.; fifteen months on staff of A. H. Allen and Partners, Sheffield, as assistant analyst; since January, 1914, to present time demonstrator in technical analysis at the Imperial College of Science and Technology; hold diploma of membership of Imperial College (D.I.C.). (*Signed by*) William A. Bone, James C. Philip, H. B. Baker, P. W. Robertson, H. F. Harwood, A. T. King.

SMITH, GEORGE, M.Sc., 33, Queen Street, Gt. Harwood, Lancs. Second class mechanic, R.N. (engaged on chemical work). Three years student in Honours School of Chemistry, Manchester University; B.Sc., 1916; research student on war-work, 1916–17; member of coal-tar staff, M. of M., 1917–18. (*Signed by*) Harold B. Dixon, Arthur Lapworth, F. P. Burt, J. E. Myers, Colin Campbell, W. K. Slater.

SOUTHRON, THOMAS WILLIAM, 32, Casselden Road, Harlesden, London, N.W.10. (Present) Lieut. and inspecting ordnance officer (ammunition and explosives), A.O.D.; (civil) responsible master, Wild Street Junior Technical and Commercial, L.C.C. Institute, Kingsway, W.C. Student: Fairfield Road Science School, Bristol, 1898–1900; Clifton Laboratory, Bristol (under Dr. E. H. Cook), 1900–1905; University College, Bristol, 1905–07; followed Inter. and Degree courses in chemistry, physics, mathematics (under Dr. Travers for chemistry). Certificates of Board of Education in prac. and theoretical inorganic and organic chemistry, sound, light, and heat, magnetism and electricity, mechanics (solids and fluids), mathematics; trained certificated teacher (Board of Education). Reason for desiring admission to Society: interest in chemistry, and to secure facilities for becoming acquainted with discussions and research. (*Signed by*) W. R. Hodgkinson, Jas. H. Haynes, G. M. Norman, L. Melville Clark, R. F. Wood Smith.

STOPFORD, THOMAS RINCK, jun., "Woodbank," Macclesfield. Manager, Harrington Bone and Chemical Works, Macclesfield. Honours B.Sc. in chemistry (Manchester), 1912; M.Sc., 1913; A.I.C., 1917. (*Signed by*) Harold B. Dixon, Arthur Lapworth, F. P. Burt, W. K. Slater, Colin Campbell.

TAVROGES, JOSEPH, 36, Crafton Street, Mile End Road, London, E. 1. Works and research chemist to the British Drug Houses, Ltd. Inter B.Sc. (London), 1915, University Exhibition (Science), 1916; University scholarship

(Chemistry), 1917. Final B.Sc. Hons. Chemistry, 1st Class. At present chemist to the British Drug Houses, Ltd. Being also desirous to keep in touch with modern chemical thought. (*Signed by*) P. C. L. Thorne, H. V. A. Briscoe, Frank G. Pope, Charles A. Keane, *Henry J. S. Sand.*

TOMLINSON, WILLIAM HENRY, Law Street Turnpike, Waterfoot, near Manchester. Lieutenant, Inspecting Ordnance Officer, Army Ordnance Department. B.Sc., 1911, Victoria University (Chemistry and Physics); 1911–1913, science master, St. David's County School; 1913–1915, science master, Beverley Grammar School. (*Signed by*) John Horsfall, W. H. Templeman, W. R. Hodgkinson, E. H. Holden, G. M. Norman, L. Melville Clark.

TOWSE, WALTER, A.I.C., Woodland Villa, Glastonbury. Leather trades chemist. 1891-6, scientific training, Leeds University; 1895, hon. assistant to Professor Procter, D.Sc., F.I.C. Contribution to Society Chemical Industry on "Indian Salt Earths," or "Hide Cures." Double silver medallist in leather manufacture in City and Guilds London Institute examinations, 1895 and 1896. Sixteen years head chemist to Elswick Leather Works, Newcastle-on-Tyne. Chemist to Messrs. Clark, Son and Morland, Glastonbury, since 1917, and Messrs. C. and J. Clark, Ltd., Street (Som.). (*Signed by*) Henry R. Procter, Arthur Smithells, J. B. Cohen, P. Phillips Bedson, J. T. Dunn.

TRYHORN, FREDERICK GERALD, 45, Hallville Road, Mossley Hill, Liverpool. Research chemist. B.Sc. 1st Division, 1st Class Hons. Chemistry, 1914, University of Liverpool. M.Sc. for research, 1915. Analyst on staff of Deputy Inspector High Explosives, Liverpool area, 1915–17. Assistant chemist, Government Rolling Mills, Southampton, 1917. At present Hydrogen Officer, Pembroke Air Station. Elected to A.I.C., 1918. Publications: contributions to scientific journals. (*Signed by*) E. C. C. Baly, Robert Robinson, W. C. McC. Lewis, F. C. Guthrie, H. H Froysell.

WEBB, HENRY MARSHALL, 63, Lancaster Gate, W. 2. B.Sc. Lond., A.I.C. Professional education at King's College, London. Am desirous of being elected to the Chemical Society so that I may have the use of the Library and receive the Journals. (*Signed by*) John M. Thomson, Herbert Jackson, Patrick H. Kirkaldy, Henry L. Smith, Leonard E. Hinkel.

WESTON, PERCY WILLIAM, 59, Grafton Street, Manchester, S.E. Proprietor and chemist of the Disincrustant Marseillais Co. I was articled pupil or apprentice to Mr. J. H. Lester, M.Sc., F.I.C., and have worked on oils and fats under Mr. Hurst, F.C.S. I was employed as chemist by the Disincrustant Marseillais Co., Manchester, from 1905 to 1914, when I became proprietor. I desire to join the Chemical Society in order to keep up to date in the chemistry of water as used for commercial purposes, with special reference to incrustation, in addition to keeping in touch with the progress of, and new discoveries in, the chemical world. (*Signed by*) Harry Brindle, Charles Turner, B. G. Hough, *W. Smith, E. J. Wilson.*

WHITE, GERALD NOEL, 15, West End Avenue, Pinner, Middlesex. Research chemist. Bachelor of Science, 2nd Class Honours, 1913. Associate of Institute of Chemistry, 1918. Tuffnell Scholar 1912–14. Senior demonstrator at University College, London, in organic and inorganic chemistry, 1912–15; assistant, 1914–15. Chemist in Ministry of Munitions of War Department of Explosives Supply, 1915–17. Munitions Inventions Research Laboratories, 1917–18. (*Signed by*) J. R. Partington, L. J. Hudleston, Samuel Smiles, W. B. Tuck, Henry Terrey.

WHITEHEAD, SIDNEY EDWARD, 92, Bristol Street, Birmingham. Chemist and engineer assisting technical adviser, Gas Section, Dept. of Explosives

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